



Digitized by the Internet Archive
in 2009 with funding from
University of Toronto

I

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

CONDUCTED BY
SIR WILLIAM THOMSON, KNT. LL.D. F.R.S. &c.
GEORGE FRANCIS FITZGERALD, M.A. F.R.S.
AND
WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

“Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster
vilior quia ex alienis libamus ut apes.” JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

VOL. XXIX.—FIFTH SERIES.
JANUARY—JUNE 1890.

L O N D O N :

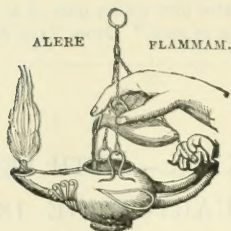
TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.

SOLD BY SIMPKIN, MARSHALL, HAMILTON, KENT, AND CO., LD.; AND WHITTAKER
AND CO.;—AND BY ADAM AND CHARLES BLACK, AND T. AND T. CLARK,
EDINBURGH; SMITH AND SON, GLASGOW;—HODGES, FIGGIS,
AND CO., DUBLIN;—PUTNAM, NEW YORK;—VEUVE J. ROYVEAU,
PARIS;—AND ASHER AND CO., BERLIN.

“Meditationis est perscrutari occulta ; contemplationis est admirari
perspicua Admiratio generat quæstionem, quæstio investigationem,
investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condât,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina celo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu.”

J. B. Pinelli ad Mazonium.



QC
1
P4
ser. 5
v. 29

18064
18/11/91
b.

CONTENTS OF VOL. XXIX.

(FIFTH SERIES).

NUMBER CLXXVI.—JANUARY 1890.

	Page
Lord Rayleigh on Bells.....	1
Ladislaus Natanson on the Kinetic Theory of the Phenomena of Dissociation in Gases	18
Prof. S. P. Langley and Mr. F. W. Very on the Temperature of the Moon	31
Mr. W. G. Gregory on a New Electric Radiation Meter ..	54
Mr. J. Enright on Electrifications due to the Contact of Gases with Liquids	56
Mr. Herbert Tomlinson on the Effect of Repeated Heating and Cooling on the Electrical Resistance of Iron	77
Prof. Tait on the Importance of Quaternions in Physics	84
Prof. T. Carnelley on an Approximate Algebraic Expression of the Periodic Law of the Chemical Elements. (Plate I.) ..	97
Mr. A. L. Selby on two Pulsating Spheres in a Liquid	113
H. Nagaoka on Transient Electric Current produced by suddenly twisting Magnetized Iron and Nickel Wires. With Note by Sir W. Thomson. (Plate II.)	123
Proceedings of the Geological Society :—	
Mons. F. M. Corpi on the Catastrophe of Kantzorik, Armenia	133
Mr. R. N. Worth on the Igneous Constituents of the Triassic Breccias and Conglomerates of South Devon .	134
Capt. A. W. Stiffe on the Glaciation of parts of the Valleys of the Jhelam and Sind Rivers, Kashmir	135
The Magnetism of Nickel and Tungsten Alloys, by John Trowbridge and Samuel Sheldon	136
Note on the Application of Hydraulic Power to Mercurial Pumps, by Rev. Frederick J. Smith	138
On Evaporation and Solution as Processes of Diffusion, by Prof. J. Stefan	139
On the Changes of Temperature resulting from the Torsion and Detorsion of Metal Wires, by Dr. A. Wassmuth	140

NUMBER CLXXVII.—FEBRUARY.

	Page
Mr. Carl Barus on the Pressure-Variations of certain High-Temperature Boiling-Points	141
Mr. Shelford Bidwell on the Electrification of a Steam-jet ..	158
Prof. Hermann Karsten on the Geological Age of the Mountains of Santa Marta	163
Mr. James C. McConnel on Diffraction-Colours, with special reference to Coronæ and Iridescent Clouds	167
Lord Rayleigh on the Vibrations of an Atmosphere	173
Eric Gerard on a Process of Plotting Curves by the Aid of Photography	180
Mr. Arthur Schuster on the Disruptive Discharge of Electricity through Gases	182
Mr. C. A. Carus-Wilson on the Behaviour of Steel under Mechanical Stress. (Plates III.-V.)	200
Prof. A. Gray on Sensitive Galvanometers	208
Notices respecting New Books :—	
Rev. O. Fisher's Physics of the Earth's Crust	211
On the Resistance of Hydrogen and other Gases to the Current and to Electrical Discharges, and on the Heat developed in the Spark, by E. Villari.....	214
Further Investigations on the Inert Space in Chemical Reactions, by O. Liebreich	216
Lecture Experiment to prove the Existence of the Direct and Inverse Extra Currents, by M. C. Daguenet	216

NUMBER CLXXVIII.—MARCH.

Mr. A. W. Flux on the Form of Newton's Rings	217
Prof. John Perry on Twisted Strips	244
Mr. Spencer U. Pickering on a New Form of Mixing-Calorimeter. (Plate VII.).....	247
H. E. J. G. du Bois on Kerr's Magneto-optic Phenomenon ..	253
Mr. Fred. T. Trouton on the Acceleration of Secondary Electromagnetic Waves. (Plate VI.)	268
Sir William Thomson on the Time-Integral of a Transient Electromagnetically Induced Current	276
Proceedings of the Geological Society :—	
Prof. J. Prestwich on the Relation of the Westleton Beds or 'Pebbly Sands' of Suffolk to those of Norfolk	280
Prof. C. Lloyd Morgan on the Pebidian Volcanic Series of St. Davids	282
Prof. T. G. Bonney on the Crystalline Schists and their Relation to the Mesozoic Rocks in the Lepontine Alps	284

	Page
Messrs. G. A. J. Cole and J. W. Gregory on the Varioritic Rocks of Mont-Genève	286
Prof. John W. Judd on the Propylites of the Western Isles of Scotland, and their Relations to the Andesites and Diorites of the District	287
Note on the Gradual Alteration in Glass produced by altering its Temperature a few Degrees, by Spencer U. Pickering..	289
On a Telethermometer, by Prof. Dr. J. Puluj	291
On the Measurement of Electromotive Contact Forces of Metals in Different Gases by Means of the Ultra-Violet Rays, by A. Righi.....	291
Mr. Enright's Experiments, by Oliver J. Lodge.....	292

NUMBER CLXXIX.—APRIL.

H. E. J. G. du Bois on Magnetization in Strong Fields at Different Temperatures. (Plate VIII.)	293
Messrs. J. S. Haldane and M. S. Pembrey on an Improved Method of Determining Moisture and Carbonic Acid in Air	306
Dr. J. R. Rydberg on the Structure of the Line-Spectra of the Chemical Elements	331
Mr. Carl Barus on the Change of the Order of Absolute Viscosity encountered on passing from Fluid to Solid.....	337
Profs. T. Gray and C. L. Mees on the Effect of Permanent Elongation on the Cross Section of Hard-drawn Wires....	355
Prof. J. J. Thomson on the Passage of Electricity through Hot Gases	358
Prof. Wyndham R. Dunstan and Mr. T. S. Dymond on an Apparatus for the Distillation of Mercury in a Vacuum ..	367
Notices respecting New Books:—	
Transactions of the Edinburgh Geological Society, Vol. VI.	
Part I.	372
On Electrical Vibrations in Straight Conductors, by Prof. J. Stefan.....	373
Electrical Vibrations in Rarefied Air without Electrodes, by James Moser	375
On the Formation of Ozone by the Contact of Air with Ignited Platinum, and on the Electrical Conductivity of Air ozonized by Phosphorus, by Profs. Elster and Geitel	376
Note in Connexion with Dropping-Mercury Electrodes, by J. Brown	376

NUMBER CLXXX.—MAY.

	Page
Rev. Frederick J. Smith on a New Form of Electric Chronograph. (Plate IX.)	377
Mr. Ward Coldridge on the Electrical and Chemical Properties of Stannic Chloride; together with the Bearing of the Results therein obtained on the Problems of Electrolytic Conduction and Chemical Action.—Part I. Experimental Observations.	383
Mr. Herbert Tomlinson on the Villari Critical Points of Nickel and Iron	394
Dr. G. Gore on a New Method and Department of Chemical Research	401
Mr. Spencer U. Pickering on the Nature of Solutions	427
Mr. T. Mather on the Shape of Movable Coils used in Electrical Measuring-Instruments	434
Mr. Shelford Bidwell on the Magnetization of Iron in Strong Fields	440
Prof. J. J. Thomson on the Passage of Electricity through Hot Gases	441
Notices respecting New Books:—	
Dr. G. Chrystal's Algebra: an elementary Textbook for the higher classes of Secondary Schools and for Colleges	449
On Electrical Oscillations in Straight Conductors, by Prof. Stefan	450
On the Oscillations of Periodically Heated Air, by Dr. Margules	452

NUMBER CLXXXI.—JUNE.

Mr. James C. McConnel on the Theory of Fog-Bows. (Plate X.)	453
Prof. C. Runge on a Method of Discriminating Real from Accidental Coincidences between the Lines of Different Spectra	462
Dr. G. Johnstone Stoney on Texture in Media, and on the Non-existence of Density in the Elemental Æther.....	467
Prof. W. Ostwald on the Theory of Dropping Electrodes.—Reply to Mr. Brown.....	479
Mr. Ward Coldridge on the Electrical and Chemical Properties of Stannic Chloride; together with the Bearing of the Results therein obtained on the Problems of Electrolytic Conduction and Chemical Action.—Part II. Theoretical Considerations	480
Mr. Spencer U. Pickering on the Theory of Osmotic Pressure and its bearing on the Nature of Solutions.....	490

	Page
Rev. Frederick J. Smith on a Mercury-still for the Rapid Distillation of Mercury in a Vacuum	501
Mr. Charles A. Carus-Wilson on the Distribution of Flow in a Strained Elastic Solid	503
Prof. R. Threlfall on Sensitive Galvanometers	508
M. F. Osmond's Considerations on Permanent Magnetism ..	511
Notices respecting New Books:—	
Dr. A. Irving's Chemical and Physical Studies in the Metamorphism of Rocks	514
The Radiant Energy of the Standard Candle; Mass of Meteors, by C. C. Hutchins.....	518
Observations on Atmospheric Electricity in the Tropics, by F. Exner	520
Index.....	521

PLATES.

- I. Illustrative of Prof. Carnelley's Paper on an Approximate Algebraic Expression of the Periodic Law of the Chemical Elements.
- II. Illustrative of H. Nagaoka's Paper on Transient Electric Current produced by suddenly twisting Iron and Nickel Wires.
- III.-V. Illustrative of Mr. C. A. Carus-Wilson's Paper on the Behaviour of Steel under Mechanical Stress.
- VI. Illustrative of Mr. Fred. T. Trouton's Paper on the Acceleration of Secondary Electromagnetic Waves.
- VII. Illustrative of Mr. Spencer U. Pickering's Paper on a New Form of Mixing-Calorimeter.
- VIII. Illustrative of H. E. J. G. du Bois's Paper on Magnetization in Strong Fields at Different Temperatures.
- IX. Illustrative of Rev. F. J. Smith's Paper on a new Form of Electric Chronograph.
- X. Illustrative of Mr. J. C. McConnel's Paper on the Theory of Fog-Bows.

ERRATA.

Page 10, column 1, for f''' read f''

"	"	2,	"	d'''	"	d''
"	"	3,	"	f'	"	f''
"	"	4,	"	d'	"	d''
"	"	7,	"	g'	"	g''
"	"	8,	"	g'	"	g''

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

JANUARY 1890.

I. *On Bells.* By Lord RAYLEIGH, *Sec. R.S.**

THE theory of the vibrations of bells is of considerable difficulty. Even when the thickness of the shell may be treated as very small, as in the case of air-pump receivers, finger-bowls, claret glasses, &c., the question has given rise to a difference of opinion. The more difficult problem presented by church bells, where the thickness of the metal in the region of the *sound-bow* (where the clapper strikes) is by no means small, has not yet been attacked. A complete theoretical investigation is indeed scarcely to be hoped for; but one of the principal objects of the present paper is to report the results of an experimental examination of several church bells, in the course of which some curious facts have disclosed themselves.

In practice bells are designed to be symmetrical about an axis, and we shall accordingly suppose that the figures are of revolution, or at least differ but little from such. Under these circumstances the possible vibrations divide themselves into classes, according to the number of times the motion repeats itself round the circumference. In the gravest mode, where the originally circular boundary becomes elliptical, the motion is once repeated, that is it occurs *twice*. The number of nodal meridians, determined by the points where the circle intersects the ellipse, is *four*, the meridians corresponding (for example) to longitudes 0° and 180° being reckoned separately. In like manner we may have 6, 8, 10 ..

* Communicated by the Author.

nodal meridians, corresponding to 3, 4, 5 . . . cycles of motion. A class of vibrations is also possible which are symmetrical about the axis, the motion at any point being either in or perpendicular to the meridional plane. But these are of no acoustical importance.

The meaning here attached to the word *nodal* must be carefully observed. The meridians are not nodal in the sense that there is no motion, but only that there is no motion *normal to the surface*. This can be best illustrated by the simplest case, that of an infinitely long thin circular cylinder vibrating in two dimensions*. The graver vibrations are here purely flexural, the circumference remaining everywhere unstretched during the motion. If we fix our attention upon one mode of vibration of n cycles, the motion at the surface is usually both radial and tangential. There are, however, $2n$ points distributed at equal intervals where the motion is purely tangential, and other $2n$ points, bisecting the intervals of the former, where the motion is purely radial. There are thus no places of complete rest; but the first set of points, or the lines through them parallel to the axis, are called nodal, in the sense that there is at these places no normal motion.

The two systems of points have important relations to the place where the vibrations are excited. "When a bell-shaped body is sounded by a blow, the point of application of the blow is a place of maximum normal motion of the resulting vibrations, and the same is true when the vibrations are excited by a violin-bow, as generally in lecture-room experiments. Bells of glass, such as finger-glasses, are, however, more easily thrown into regular vibration by friction with the wetted finger carried round the circumference. The pitch of the resulting sound is the same as that elicited by a tap with the soft part of the finger; but inasmuch as the tangential motion of a vibrating bell has been very generally ignored, the production of sound in this manner has been felt as a difficulty. It is now scarcely necessary to point out that the effect of the friction is in the first instance to excite tangential motion, and that the point of application of the friction is the place where the tangential motion is greatest, and therefore where the normal motion vanishes"†.

When the symmetry is complete, the system of nodal meridians has no fixed position, and may adapt itself so as to suit the place at which a normal blow is delivered. If the

* 'Theory of Sound,' § 232.

† 'Theory of Sound,' § 234. That the rubbing finger and the violin-bow must be applied at different points in order to obtain the same vibration was known to Chladni.

point of application of the blow be conceived to travel round a circle symmetrical with respect to the axis, say, for brevity, a circle of *latitude*, the displacement will make no difference to the vibration considered as a whole, but the effect upon an observer who retains a fixed position will vary. If the bell be situated in an open space, or if the ear of the observer be so close that reflexions are relatively unimportant, the sound disappears as nodes pass by him, swelling to a maximum when the part nearest to the ear is one of the places of maximum normal motion, which for brevity we will call *loops*. In listening to a particular note it would thus be possible to determine the number of nodal meridians by watching the variations of intensity which occur as the place of the blow travels round a circle of latitude.

In practice the symmetry is seldom so complete that this account of the matter is sufficient. Theoretically the slightest departure from symmetry will in general render determinate the positions of the nodal systems. For each number of cycles n , there is one determinate mode of vibration with $2n$ nodes and $2n$ intermediate loops, and a second determinate mode in which the nodes and loops of the first mode exchange functions. Moreover the frequencies of the vibrations in the two modes are slightly different.

In accordance with the general theory, the vibrations of the two modes as dependent upon the situation and magnitude of the initiating blow are to be considered separately. The vibrations of the first mode will be excited, unless the blow occur at a node of this system; and in various degrees, reaching a maximum when the blow is delivered at a loop. The intensity, as appreciated by an observer, depends also upon the position of his ear, and will be greatest when a loop is immediately opposite. As regards the vibrations of the second mode, they reach a maximum when those of the first mode disappear, and conversely.

Thus in the case of n cycles, there are $2n$ places where the first vibration is not excited and $2n$ places, midway between the former, where the second vibration is not excited. At all $4n$ places the resulting sound is free from beats. In all other cases both kinds of vibration are excited, and the sound will be affected by beats. But the prominence of the beats depends upon more than one circumstance. The intensities of the two vibrations will be equal when the place of the blow is midway between those which give no beats. But it does not follow that the audible beats are then most distinct. The condition to be satisfied is that the intensities shall be equal as they reach the ear, and this will depend upon the situation

of the observer as well as upon the vigour of the vibrations themselves. Indeed, by suitably choosing the place of observation it would be theoretically possible to obtain beats with perfect silences, wherever (in relation to the nodal systems) the blow may be delivered.

There will now be no difficulty in understanding the procedure adopted in order to fix the number of cycles corresponding to a given tone. If, in consequence of a near approach to symmetry, beats are not audible, they are introduced by suitably loading the vibrating body. By tapping cautiously round a circle of latitude the places are then investigated where the beats disappear. But here a decision must not be made too hastily. The inaudibility of the beats may be favoured by an unsuitable position of the ear, or of the mouth of the resonator in connexion with the ear. By travelling round, a situation is soon found where the observation can be made with the best advantage. In the neighbourhood of the place where the blow is being tried there is a loop of the vibration which is most excited and a (coincident) node of the vibration which is least excited. When the ear is opposite to a node of the first vibration, and therefore to a loop of the second, the original inequality is redressed, and distinct beats may be heard even although the deviation of the blow from a nodal point may be very small. The accurate determination in this way of two consecutive places where no beats are generated is all that is absolutely necessary. The ratio of the entire circumference of the circle of latitude to the arc between the points represents $4n$, that is four times the number of cycles. Thus, if the arc between consecutive points proved to be 45° , we should infer that we were dealing with a vibration of two cycles—the one in which the deformation is elliptical. As a greater security against error, it is advisable in practice to determine a larger number of points where no beats occur. Unless the deviation from symmetry be considerable, these points should be uniformly distributed along the circle of latitude*.

In the above process for determining nodes we are supposed to hear distinctly the tone corresponding to the vibration under investigation. For this purpose the beats are of assistance in directing the attention; but with the more difficult subjects, such as church bells, it is advisable to have recourse to resonators. A set of Helmholtz's pattern, manufactured by Koenig, are very convenient. The one next higher

* The bells, or gongs, as they are sometimes called, of striking clocks often give disagreeable beats. A remedy may be found in a suitable rotation of the bell about its axis.

in pitch to the tone under examination is chosen and tuned by advancing the finger across the aperture. Without the security afforded by resonators, the determination of the octave is in my experience very uncertain. Thus pure tones are often estimated by musicians an octave too low.

Some years ago I made observations upon the tones of various glass bells, of which the walls were tolerably thin. A few examples may be given :—

- | | | | |
|------|----------|----------|-----------|
| I. | c' , | $e''b$, | $e'''z$. |
| II. | a , | $e''z$, | b'' . |
| III. | $f''z$, | b'' . | |

The value of n for the gravest tone is 2, for the second 3, and for the third 4. On account of the irregular shape and thickness only a very rough comparison with theory is possible; but it may be worth mention that for a thin uniform hemispherical bell the frequencies of the three slowest vibrations should be in the ratios

$$1 : 2.8102 : 5.4316 :$$

so that the tones might be

$$c, f'z, f'', \text{approximately.}$$

More recently, through the kindness of Messrs. Mears and Stainbank, I have had an opportunity of examining a so-called hemispherical metal bell, weighing about 3 cwt. A section is shown in fig. 1. Four tones could be plainly heard,

$$eb, f'z, e'', b'',$$

the pitch being taken from a harmonium. The gravest tone

Fig. 1.



has a long duration. When the bell is struck by a hard body, the higher tones are at first predominant, but after a time they die away, and leave c in possession of the field. If the striking body be soft, the original preponderance of the higher elements is less marked.

By the method above described there was no difficulty in showing that the four tones correspond respectively to $n=2, 3, 4, 5$. Thus for the gravest tone the vibration is elliptical with 4 nodal meridians, for the next tone there are 6 nodal meridians, and so on. Tapping along a meridian showed that the sounds became less clear as the edge was departed from, and this in a continuous manner with no suggestion of a nodal circle of latitude.

A question, to which we shall recur in connexion with church bells, here suggests itself. Which of the various co-existing tones characterizes the pitch of the bell as a whole? It would appear to be the third in order, for the founders give the pitch as *E nat*.

My first attempts upon church bells were made in September 1879, upon the second bell (reckoned from the highest) of the Terling peal; and I was much puzzled to reconcile the pitch of the various tones, determined by resonators, with the effective pitch of the bell, when heard from a distance in conjunction with the other bells of the peal. There was a general agreement that the five notes of the peal were

$$\sharp, \quad g\sharp, \quad a\sharp, \quad b, \quad c\sharp,$$

according to harmonium pitch, so that the note of the second bell was *b*. A tone of pitch $a\sharp$ could be heard, but at that time nothing coincident with *b* or its octaves. Subsequently, in January 1880, the *b* was found among the tones of the bell, but at much higher pitch than had been expected. The five gravest tones were determined to be

$$d', \quad a\sharp, \quad d'', \quad g\sharp +, \quad b'';$$

so that the nominal note of the bell agreed with the fifth component tone, and with no graver one. The octaves are here indicated by dashes in the usual way, the *d'* immediately below the *d'* being the middle *c* of the musical scale.

Attempts were then made to identify the modes of vibration corresponding to the various tones, but with only partial success. By tapping round the sound-bow it appeared that the minima of beats for *d'* occurred at intervals equal to $\frac{1}{8}$ of the circumference, indicating that the deformation in this mode was elliptical ($n=2$), as had been expected. In like manner $g\sharp +$ gave $n=3$; but on account of the difficulty of experimenting in the belfry, the results were not wholly satisfactory, and I was unable to determine the modes for the other tones. One observation, however, of importance could be made. All five tones were affected with beats, from which

it was concluded that none of them could be due to symmetrical vibrations, as, till then, had been thought not unlikely.

Nothing further worthy of record was effected until last year, when I obtained from Messrs. Mears and Stainbank the loan of a 6-cwt. bell. Hung in the laboratory at a convenient height, and with freedom of access to all parts of the circumference, this bell afforded a more convenient subject for experiment, and I was able to make the observations by which before I had been baffled. Former experience having shown me the difficulty of estimating the pitch of an isolated bell, I was anxious to have the judgment of the founders expressed in a definite form, and they were good enough to supply me with a fork tuned to the pitch of the bell. By my harmonium the fork is d'' .

By tapping the bell in various places with a hammer or mallet, and listening with resonators, it was not difficult to detect 6 tones. They were identified with the following notes of the harmonium* :—

$$\begin{array}{cccccc} e', & c'', & f'' +, & b'' \flat, & d''', & f'''. \\ (4) & (4) & (6) & (6) & (8) & \end{array}$$

As in the former case, the nominal pitch is governed by the fifth component tone, whose pitch is, however, an octave higher than that of the representative fork. It is to be understood, of course, that each of the 6 tones in the above series is really double, and that in some cases the components of a pair differ sufficiently to give rise to somewhat rapid beats. The sign + affixed to f'' indicates that the tone of the bell was decidedly sharp in comparison with the note of the instrument.

I now proceeded to determine, as far as possible, the characters of the various modes of vibration by observations upon the dependence of the sounds upon the place of tapping in the manner already described. By tapping round a circle of latitude it was easy to prove that for (each of the approximately coincident tones of) e' there were 4 nodal meridians. Again, on tapping along a meridian to find whether there were any nodal circles of latitude, it became evident that there were none such. At the same time differences of intensity were observed. This tone is more fully developed

* In comparisons of this kind the observer must bear in mind the highly compound character of the notes of a reed instrument. It is usually a wise precaution to ascertain that a similar effect is not produced by the octave (or twelfth) above.

when the blow is delivered about midway between the crown and rim of the bell than at other places.

The next tone is c'' . Observation showed that for this vibration also there are four, and but four, nodal meridians. But now there is a well-defined nodal circle of latitude, situated about a quarter of the way up from the rim towards the crown. As heard with the resonator, this tone disappears when the blow is accurately delivered at some point of this circle, but revives with a very small displacement on either side. The nodal circle and the four meridians divide the surface into segments, over each of which the normal motion is of one sign.

To the tone f'' correspond 6 nodal meridians. There is no well-defined nodal circle. The sound is indeed very faint, when the tap is much removed from the sound-bow; it was thought to fall to a minimum when the tap was about halfway up.

The three graver tones are heard loudly from the sound-bow. But the next in order, $b''p$, is there scarcely audible, unless the blow be delivered to the rim itself in a tangential direction. The maximum effect occurs at about halfway up. Tapping round the circle, we find that there are 6 nodal meridians.

The fifth tone, d''' , is heard loudly from the sound-bow, but soon falls off when the locality of the blow is varied, and in the upper three fourths of the bell it is very faint. No distinct circular node could be detected. Tapping round the circumference showed that there were here 8 nodal meridians.

The highest tone recorded, f''' , was not easy of observation, and I did not succeed in satisfying myself as to the character of the vibration. The tone was perhaps best heard when the blow was delivered at a point a little below the crown.

All the above tones, except f'' , were tolerably close in pitch to the corresponding notes of the harmonium.

Although the above results seemed perfectly unambiguous, I was glad to have an opportunity of confirming them by examination of another bell. This was afforded by a loan of a bell cast by Taylor, of Loughborough, and destined for the church of Ampton, Suffolk, where it now hangs. Its weight is somewhat less than 4 cwt., and the nominal pitch is d . The observations were entirely confirmatory of the results obtained from Messrs. Mears's bell. The tones were

$$\begin{array}{cccccc} d^p-2, & d''-6, & f''+4, & b''p-b'', & d''', & g'''; \\ (4) & (4) & (6) & (6) & (8) & \end{array}$$

the correspondence between the order of the tone and the number of nodal meridians being as before. In the case of d'' there was the same well-defined nodal circle. The highest

tone, ϕ''' , was but imperfectly heard, and no investigation could be made of the corresponding mode of vibration.

In the specification of pitch the numerals following the note indicate by how much the frequency for the bell differed from that of the harmonium. Thus the gravest tone ϕ gave 2 beats per second, and was flat. When the number exceeds 3, it is the result of somewhat rough estimation and cannot be trusted to be quite accurate. Moreover, as has been explained, there are in strictness two frequencies under each head, and these often differ sensibly. In the case of the 4th tone, $\psi''\phi - \psi''$ means that, as nearly as could be judged, the pitch of the bell was midway between the two specified notes of the harmonium.

The sounds of bells may be elicited otherwise than by blows. Advantage may often be taken of the response to the notes of the harmonium, to the voice, or to organ-pipes sounded in the neighbourhood. In these cases the subsequent resonance of the bell has the character of a pure tone. Perhaps the most striking experiment is with a tuning-fork. A massive ϕ (ϕ on the $\phi=256$ scale) fork, tuned with wax, and placed upon the waist of the Ampton bell, called forth a magnificent resonance, which lasted for some time after removal and damping of the fork. The sound is so utterly unlike that usually associated with bells that an air of mystery envelops the phenomenon. The fork may be excited either by a preliminary blow upon a pad (in practice it was the bent knee of the observer), or by bowing when in contact with the bell. In either case the adjustment of pitch should be very precise, and it is usually necessary to distinguish the two nearly coincident tones of the bell. One of these is to be chosen, and the fork is to be held near a loop of the corresponding mode of vibration. In practice the simplest way to effect the tuning is to watch the course of things after the vibrating fork has been brought into contact with the bell. When the tuning is good the sound swells continuously. Any beats that are heard must be gradually slowed down by adjustment of wax, until they disappear.

Observations upon the two bells in the laboratory having settled the modes of vibration corresponding to the five gravest tones, other bells of the church pattern can be sufficiently investigated by simple determinations of pitch. I give in tabular form results of this kind for a Belgian bell, kindly placed at my disposal by Mr. Haweis, and for the five bells of the Terling peal. For completeness' sake the Table includes also the corresponding results for the two bells already described.

Mears, 1888.	Ampton, 1888.	Belgian Bell.	Terling (5), Osborn, 1783.	Terling (4), Mears, 1810.	Terling (3), Grave, 1623.	Terling (2), Gardner, 1723.	Terling (1), Warner, 1803.
Actual Pitch by Harmonium.							
c'	$c'b-2$	$d'-4$	$g-3$	$a+3$	$a\sharp+3$	$d'-6$	$d'+2$
c''	$d''-6$	$c''\sharp-d''$	$g'-4$	$g'\sharp-4$	$a'+6$	$a'\sharp-5$	$b'+2$
$f''' +$	$f''+4$	$f'+1$	$a'+6$	$b'+6$	$c''\sharp+4$	$d''+8$	c''
$b''b$	$b''b-b''$	$a''-6$	$d'-3$	$d'\sharp-c''$	$c''+6$	$g'\sharp+(10)$	$g'\sharp+4$
d'''	d'''	$f''\sharp-2$	$g'\sharp-6$	$a''\sharp$	$b''+2$	$c''\sharp+3$
f'''	g'''						
Pitch referred to fifth tone as c .							
d	$c\sharp-2$		$c\sharp-3$	$c\sharp+3$	$c+3$	$c b-6$	$c\sharp+2$
$b b$	$c-6$		$c\sharp-4$	$c-4$	$b b+6$	$b-5$	$b b+2$
$c b +$	$c b+4$		$c b+6$	$c b+6$	$c b+4$	$c b+8$	$c b$
$a b$	$a b-a$		$a b-3$	$g'-g\sharp$	$f\sharp+6$	$a+8$	$g'+4$
c	c		$c-2$	$c-6$	c	$c+2$	$c+3$

It will be seen that in every case where the test can be applied, it is the fifth tone in order which agrees with the nominal pitch of the bell. The reader will not be more surprised at this conclusion than I was, but there seems to be no escape from it. Even apart from estimates of pitch, an examination of the tones of the bells of the Terling peal proves that it is only from the third and fifth tones that a tolerable diatonic scale can be constructed. Observations in the neighbourhood of bells do not suggest any special predominance of the fifth tone, but the effect is a good deal modified by distance.

It has been suggested, I think by Helmholtz, that the aim of the original designers of bells may have been to bring into harmonic relations tones which might otherwise cause a disagreeable effect. If this be so, the result cannot be considered very successful. A glance at the Table shows that in almost every case there occur intervals which would usually be counted intolerable, such as the false octave. Terling (5) is the only bell which avoids this false interval between the two first tones; but the improvement here shown in this respect still leaves much to be desired, when we consider the relation of these two tones to the fifth tone, and the nominal pitch of the bell. Upon the assumption that the nominal pitch is governed by that of the fifth tone, I have exhibited in the second part of the above Table the relationship in each case of the various tones to this one.

One of my objects in this investigation having been to find out, if possible, wherein lay the difference between good and bad bells, I was anxious to interpret in accordance with my results the observations of Mr. Haweis, who has given so much attention to the subject. The comparison is, however, not free from difficulty. Mr. Haweis says* :—"The true Belgian bell when struck a little above the rim gives the dominant note of the bell; when struck two-thirds up it gives the third; and near the top the fifth; and the 'true' bell is that in which the third and fifth (to leave out a multitude of other partials) are heard in right relative subordination to the dominant note."

If I am right in respect of the dominant note, the *third* spoken of by Mr. Haweis must be the minor third (or, rather, major sixth) presented by the tone third in order, which it so happens is nearly the same interval in all cases. The only *fifth* which occurs is that of the tone fourth in order. Thus, according to Mr. Haweis's views, the best bell in the series would be Terling (1), for which the minor chord of the last

* 'Times,' October 29, 1878.

three tones is very nearly true. It must be remarked, however, that the tone fourth in order is scarcely heard in the normal use of the bell, so that its pitch can hardly be of importance directly, although it may afford a useful criterion of the character of the bell as a whole. It is evident that the first and second tones of Terling (1) are quite out of relation with the higher ones. If the first could be depressed a semitone and the second raised a whole tone, harmonic relations would prevail throughout.

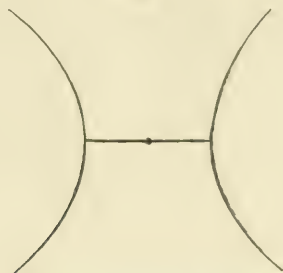
Judging from the variety presented in the Table, it would seem not a hopeless task so to construct a bell that all the important tones should be brought into harmonic relation; but it would require so much tentative work that it could only be undertaken advantageously by one in connexion with a foundry. As to what advantage would be gained in the event of success, I find it difficult to form an opinion. All I can say is that the dissonant effect of the inharmonious intervals actually met with is less than one would have expected from a musical point of view; although the fact is to a great extent explained by Helmholtz's theory of dissonance.

One other point I will touch upon, though with great diffidence. If there is anything well established in theoretical acoustics it is that the frequencies of vibration of similar bodies formed of similar material are inversely as the linear dimensions—a law which extends to *all* the possible modes of vibration. Hence, if the dimensions are halved, all the tones should rise in pitch by an exact octave. I have been given to understand, however, that bells are not designed upon this principle of similarity, and that the attempt to do so would result in failure. It is just possible that differences in cooling may influence the hardness, and so interfere with the similarity of corresponding parts, in spite of uniformity in the chemical composition of the metal; but this explanation does not appear adequate. Can it be that when the scale of a bell is altered it is desirable at the same time to modify the relative intensities, or even the relative frequencies, of the various partials?

Observations conducted about ten years ago upon the manner of bending of bell-shaped bodies—waste-paper baskets and various structures of flexible material—led me to think that these shapes were especially stiff as regards the principal mode of bending (with four nodal meridians) to forces applied normally and near the rim, and that possibly one of the objects of the particular form adopted for bells might be to diminish the preponderance of the gravest tone. To illustrate this I made calculations, according to the theory of the paper

already alluded to, of the deformation by pure bending of thin shells in the form of hyperboloids of revolution, and in certain composite forms built up of cylinders and cones so as to represent approximately the actual shape of bells. In the case of the hyperboloid of one sheet (fig. 2), completed by a

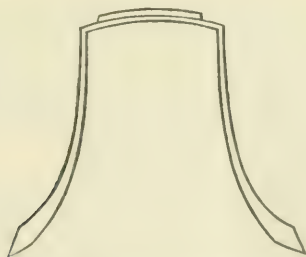
Fig. 2.



crown in the form of a circular disk through the centre, and extending across the aperture, it appeared that there was no nodal circle for $n=2$. The investigation is appended to this paper.

The composite forms, figs. 4 and 5, represent the actual bell (fig. 3*) as nearly as may be. At the top is a circular disk,

Fig. 3.



and to this is attached a cylindrical segment. The expanding part of the bell is represented by one (fig. 4), or with better approximation by two (fig. 5), segments of cones. The calculations are too tedious to be reproduced here, but the results are shown upon the figures. In both cases there is a circular node N for $n=2$, not far removed from the rim, and in fig. 5 very nearly at the place which represents the sound-bow of an actual bell. In the latter case there is a node N' for $n=3$ near the middle of the intermediate conical segment.

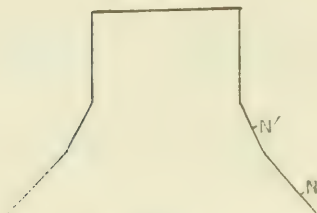
* Copied from Zamminer, *Die Musik und die musikalischen Instrumente*. Giessen, 1855.

The nodal circle for $n=2$ has been verified experimentally upon a bell constructed of thin sheet zinc in the form of fig. 5. The gravest note, $G\sharp$, and the corresponding mode of vibration, could be investigated exactly in the manner already described. In each mode of this kind there were four nodal

Fig. 4.



Fig. 5.



meridians, and a very well defined nodal circle. The situation of this circle was not quite so low as according to calculation; it was almost exactly in the middle of the lower conical segment. By merely handling the model it was easy to recognize that it was stiff to forces applied at N , but flexible higher up, in the neighbourhood of N' .

It is clear that the actual behaviour of a church bell differs widely from that of a bell infinitely thin; and that this should be the case need not surprise us when we consider the actual ratio of the thickness at the sound-bow to the interval between consecutive nodal meridians. I think, however, that the form of the bell does really tend to render the gravest tone less prominent.

APPENDIX.

On the Bending of a Hyperboloid of Revolution.

The deformation of the general surface of revolution was briefly treated in a former paper *. The point whose original

* "On the Infinitesimal Bending of Surfaces of Revolution," Proc. Math. Soc. xiii. p. 4 (1881).

cylindrical coordinates are z, r, ϕ , is supposed to undergo such a displacement that its coordinates become

$$z + \delta z, \quad r + \delta r, \quad \phi + \delta \phi.$$

The altered value $(ds + d\delta s)$ of the element of length traced upon the surface is given by

$$(ds + d\delta s)^2 = (dz + d\delta z)^2 + (r + \delta r)^2 (\delta \phi + d\delta \phi)^2 + (dr + d\delta r)^2.$$

Hence, if the displacement be such that the element is unextended,

$$dz \, d\delta z + r^2 d\phi \, d\delta \phi + r \delta r (d\phi)^2 + dr \, d\delta r = 0.$$

Now

$$d\delta z = \frac{d\delta z}{dz} dz + \frac{d\delta z}{d\phi} d\phi,$$

$$d\delta r = \frac{d\delta r}{dz} dz + \frac{d\delta r}{d\phi} d\phi,$$

$$d\delta \phi = \frac{d\delta \phi}{dz} dz + \frac{d\delta \phi}{d\phi} d\phi;$$

and by the equation to the surface

$$dr = \frac{dr}{dz} dz + \frac{dr}{d\phi} d\phi,$$

in which, by hypothesis, $dr/d\phi = 0$. Thus

$$\begin{aligned} (dz)^2 \left\{ \frac{d\delta z}{dz} + \frac{dr \, d\delta r}{dz \, dz} \right\} + (d\phi)^2 \left\{ r^2 \frac{d\delta \phi}{d\phi} + r \delta r \right\} \\ + dz \, d\phi \left\{ \frac{d\delta z}{d\phi} + r^2 \frac{d\delta \phi}{dz} + \frac{dr \, d\delta r}{dz \, d\phi} \right\} = 0. \end{aligned}$$

If the displacement be of such a character that no line traced upon the surface is altered in length, the coefficients of $(dz)^2$, $(d\phi)^2$, $dz \, d\phi$, in the above equation, must vanish separately, so that

$$\frac{d\delta z}{dz} + \frac{dr \, d\delta r}{dz \, dz} = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$r \frac{d\delta \phi}{d\phi} + \delta r = 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{d\delta z}{d\phi} + r^2 \frac{d\delta \phi}{dz} + \frac{dr \, d\delta r}{dz \, d\phi} = 0. \quad . \quad . \quad . \quad . \quad (3)$$

From these, by elimination of δr ,

$$\frac{d\delta z}{dz} - \frac{dr}{dz} \frac{d}{dz} \left(r \frac{d\delta\phi}{dz} \right) = 0, \quad . \quad . \quad . \quad (4)$$

$$\frac{d\delta z}{d\phi} + r^2 \frac{d\delta\phi}{dz} - r \frac{dr}{dz} \frac{d^2\delta\phi}{d\phi^2} = 0; \quad . \quad . \quad . \quad (5)$$

from which again, by elimination of δz ,

$$\frac{d}{dz} \left(r^2 \frac{d\delta\phi}{dz} \right) - r \frac{d^2r}{dz^2} \frac{d^2\delta\phi}{d\phi^2} = 0. \quad . \quad . \quad . \quad (6)$$

For the purposes of the present problem we may assume that $d\phi$ varies as $\cos s\phi$, or as $\sin s\phi$; thus,

$$r^2 \frac{d}{dz} \left(r^2 \frac{d\delta\phi}{dz} \right) + s^2 r^3 \frac{d^2r}{dz^2} \delta\phi = 0 \quad . \quad . \quad . \quad (7)$$

is the equation by which the form of $\delta\phi$ as a function of z is to be determined.

When application is made to the hyperboloid of one sheet

$$\frac{r^2}{a^2} - \frac{z^2}{b^2} = 1 \quad . \quad . \quad . \quad (8)$$

we find, since

$$r \frac{dr}{dz} = \frac{a^2 z}{b^2}, \quad r^3 \frac{d^2r}{dz^2} = \frac{a^4}{b^2},$$

$$r^2 \frac{d}{dz} \left(r^2 \frac{d\delta\phi}{dz} \right) + \frac{s^2 a^4}{b^2} \delta\phi = 0. \quad . \quad . \quad . \quad (9)$$

The solution of this equation is expressed by an auxiliary variable χ , such that

$$z = b \tan \chi, \quad r = a \sec \chi \quad . \quad . \quad . \quad (10)$$

in the form

$$\delta\phi = A \cos s\chi + B \sin s\chi. \quad . \quad . \quad . \quad (11)$$

In order to verify this it is only necessary to observe that by (10)

$$r^2 \frac{d}{dz} = \frac{a^2}{b} \frac{d}{d\chi}.$$

We will now apply this solution to an inextensible surface

formed by half the hyperboloid and a crown stretching across in the plane of symmetry $z=0$ (fig. 2). The deformation of this crown can take place only in the direction perpendicular to its plane, so that $\delta r=0$, $\delta\phi=0$. These conditions must apply also to the hyperboloid at the place of attachment to the crown. Hence $\delta\phi$ must vanish with z , or, which is the same, with χ . Accordingly $A=0$ in (11); and dropping the constant multiplier we may take as the solution

$$\delta\phi = \sin s\chi \cos s\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and in correspondence therewith by (2) and (3)

$$\delta r = sr \sin s\chi \sin s\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\delta z = -\frac{a^2}{b} \{ \cos s\chi + s \tan \chi \sin s\chi \} \sin s\phi. \quad . \quad . \quad (14)$$

It is evident from these equations that, whatever may be the value of s , there is no circle of latitude over which both $\delta\phi$ (or δr) and δz vanish*. Hence there can be no circular nodal line in the absolute sense. But just as there are meridians ($\sin s\phi=0$) on which the *normal* motion vanishes, so there may be nodal circles in this more limited sense. The condition to be satisfied is obviously

$$\delta r / \delta z = dr / dz ;$$

or in the present case

$$\sin 2\chi + 2s \tan s\chi (\sin^2 \chi + b^2/a^2) = 0. \quad . \quad . \quad (15)$$

In this equation the range of χ is from 0 to $\frac{1}{2}\pi$; and thus there can be solutions only when $\tan s\chi$ is negative.

In the case $s=2$ the equation reduces to

$$1 + 2 \sin^2 \chi + 4b^2/a^2 = 0,$$

which can never be satisfied.

When $s=3$, the roots, if any, must lie between $\chi=30^\circ$ and $\chi=60^\circ$. A more detailed consideration shows that there is but one root, and that it occurs when χ is a little short of 60° .

* A corresponding proposition may be proved more generally, that is without limitation to the hyperboloid.

II. *On the Kinetic Theory of the Phenomena of Dissociation in Gases.* By LADISLAUS NATANSON*.

IT is well known that the problem of the dissociation of gaseous bodies has been successfully attacked by several physicists by thermodynamic methods. If one attempts to apply the kinetic theory, it will be found difficult to make a complete calculation without introducing certain assumptions as to the mode of combination of the atoms in gaseous molecules. Therefore the first task of the theory consists in making such assumptions as are either in agreement with experiment, or else, on the other hand, the most general possible. As this object does not appear to be sufficiently evident, I have allowed myself to enter into a more detailed consideration of a simple case.

§ 1. In the space v there are present N_1 free atoms and N_2 diatomic molecules; every atom has the same properties. The total number of atoms is $N = N_1 + 2N_2$. If m is the mass of an atom, the mass of the gas will be mN ; I shall assume henceforth that we are always dealing with unit mass. The problem which was usually considered was the determination of the ratio $\frac{N_1}{N}$ (the dissociation ratio) as a function of the pressure and temperature; and its object was attained somewhat after the following manner.

Let p_1 and p_2 denote the partial pressures of the two gases (molecular and atomic); let p be the total pressure, t the common temperature, and E_1 and E_2 the mean values of the kinetic energy of a free atom and of the centre of mass of a molecule respectively. Apart from phenomena of dissociation let both gases be considered perfect. Then we may write

$$\frac{3}{2} p_1 v = N_1 E_1; \quad \frac{3}{2} p_2 v = N_2 E_2; \quad p = p_1 + p_2, \quad \dots \quad (A)$$

Further, according to Maxwell's law, $E_1 = E_2$; and we use the magnitude of this energy as a measure of the temperature by assuming

$$E_1 = E_2 = \lambda t, \quad \dots \quad (B)$$

where λ is some constant. From (A) and (B) it will be found that

$$\frac{3}{2} p v = (N_1 + N_2) \lambda t. \quad \dots \quad (1)$$

Now let us introduce the condition for equilibrium. This

* Translated from Wiedemann's *Annalen*, xxxviii. p. 288 (1889) by James L. Howard, D.Sc.

will be reached when the number of molecules decomposed during any period of time is equal to the number formed during the same period. As shown in previous theories*, this equality is expressed by the equation

$$\frac{N_1^2 f(t)}{v} = N_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

and hence (C) expresses the condition of equilibrium. Here $f(t)$ is a function of the temperature whose form has never been successfully determined, so far as I am aware, either by kinetic or thermodynamic methods. From (1) and (C) we have further

$$p = \frac{\lambda t (N^2 - N_1^2)}{6f(t) N_1^2} = \frac{\lambda t (1 - q^2)}{6f(t) q^2}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

q denoting the dissociation ratio $\frac{N_1}{N}$. If d is the density of the partly dissociated gas, corresponding to the state q , and δ the density of the completely dissociated body, then if the formula (1) holds good, we have

$$\frac{d}{\delta} = \frac{N_1 + 2N_2}{N_1 + N_2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whence, substituting in (2),

$$p = a \frac{\delta(d - \delta)}{(2\delta - d)^2}; \quad a = \frac{2\lambda t}{3f(t)}, \quad . \quad . \quad . \quad . \quad (4)$$

which, for shortness, I shall call "Gibbs's Equation."

§ 2. Gibbs's equation has been verified by various experiments; among others by those on nitrous acid†. Since we leave the function a at present undetermined, we can prove the formula by calculating the values of the expression $p(2\delta - d)^2/(d - \delta) = a\delta$, which should be constant for each isotherm. From our data it is clearly seen that the value of a does not considerably alter along any isotherm. The constancy is of course still more perfect if we calculate (for the isotherms E, F, H, J, *loc. cit.*) the expression

* To the kinetic or partly kinetic theories belong those of van der Waals, *Verslagen en Mededeelingen d. kon. Ak. d. Wet.* [2] xv. p. 199 (1880); Boltzmann, *Wied. Ann.* xxii. p. 39 (1884); and J. J. Thomson, *Phil. Mag.* [5] xviii. p. 233 (1884). It is impossible to enter upon these theories here; I only remark that certain conclusions to which I have been led in § 3 have already been indicated by Thomson. As for the rest I cannot agree with Thomson's calculations.

† E. and L. Natanson, *Wied. Ann.* xxiv. p. 454 (1885), and xxvii. p. 606 (1886).

$p(2\delta-d)^2/(d-\delta_i)$, where δ_i may be greater or less than δ , and denotes a new isothermal constant*. Whether these critical values of the density of NO_2 are similar to the critical densities of chlorine and bromine gases (which, however, were found, not for $p=0$, but at atmospheric pressure), as Ostwald supposes †; or whether the proved deviations from Gibbs's formula are attributable wholly or partly to the imperfect nature of the gas ‡—these appear to me difficult questions to decide, inasmuch as there exists no firm basis to work upon. It suffices us, for what follows, to know that Gibbs's equation, with $f(t)$ left undetermined, is always in general agreement with experiment.

§ 3. Two atoms collide and form a molecule, which lasts for a time τ . It is required to know how often this happens during unit time in a given quantity of gas. The interval τ may depend on certain variables x, y, \dots , which we need not specify, and in unit time

$$Z\phi(x, y, \dots) dx dy \dots \quad (1)$$

collisions take place between the atoms, in such a manner that the variables lie between the limits

$$x \text{ and } x+dx; \quad y \text{ and } y+dy; \dots \quad (2)$$

Let us assume that x, y, \dots in general have values lying between the limits

$$x_0 \text{ and } x_1; \quad y_0 \text{ and } y_1; \dots \quad (3)$$

and that Z is the total number of collisions between the atoms during unit time, so that

$$\int_{x_0}^{x_1} \int_{y_0}^{y_1} \dots \phi(x, y, \dots) dx dy \dots = 1. \quad (4)$$

Let us further assume that a collision of two atoms which is included in class (2) is followed by the formation of a molecule in case x, y, \dots lie between

$$\xi_0 \text{ and } \xi_1; \quad \eta_0 \text{ and } \eta_1; \dots \quad (5)$$

(Each of these classes can also be subdivided into further simple ones.) Let us write

$$\int_{\xi_0}^{\xi_1} \int_{\eta_0}^{\eta_1} \dots \phi(x, y, \dots) dx dy \dots = \varpi, \quad (6)$$

* Cf. p. 617 of the second paper.

† Ostwald, *Lehrbuch der allg. Chemie*, ii. p. 699 (1887).

‡ Ostwald, *op. cit.* ii. p. 734; Planck, *Wied. Ann.* xxxii. p. 484 (1887); J. J. Thomson, 'Applications of Dynamics to Physics and Chemistry', p. 200.

then we can say that in unit time ϖZ molecules are created, and ϖ is the ratio of the number of associating collisions to the total number. Now let us suppose that the gas has reached a state of equilibrium as regards dissociation. During time τ ,

$$\tau Z \phi(x, y, \dots) dx dy \dots \dots \dots (7)$$

molecules of class (2) will be formed, and they will each last for a time equal to τ , or differing from it by an infinitely small quantity. Therefore there will exist at any time as many molecules of class (2) as are given by (7)*.

Hence the total number N_2 of existing molecules is

$$\left. \begin{aligned} N_2 &= Z \int_{\xi_0}^{\xi_1} \int_{\eta_0}^{\eta_1} \dots \tau \phi(x, y, \dots) dx dy \dots \\ &= \varpi Z \int_{\xi_0}^{\xi_1} \int_{\eta_0}^{\eta_1} \dots \tau \phi(x, y, \dots) dx dy \dots \\ &= \varpi Z \int_{\xi_0}^{\xi_1} \int_{\eta_0}^{\eta_1} \dots \phi(x, y, \dots) dx dy \dots \end{aligned} \right\} (8)$$

where \mathfrak{S} denotes the mean value of the interval during which a molecule remains intact.

The conditions which are necessary in order that a molecule should be formed when two atoms collide are very different, according to the assumptions made respecting the mutual actions of the atoms. As hypothesis (α) we shall designate every assumption, according to which, as the result of a collision of two atoms, two opposite cases arise: either the collision is "associating," the motion of the atom becoming a stationary one, and a molecule is formed; or else "normal," in which case the atoms rebound immediately and of their own accord, as happens in the collision of molecules in common gases. With this hypothesis (α) we must also assume at the same time, that a molecule which has once been formed cannot be decomposed of itself, but only by the action of external force. As hypothesis (β) we shall, on the contrary, designate any assumption in which the above distinction is wanting: two colliding atoms will sooner or later leave each other; only the interval during which they form a system can, according to the circumstances of the collision, be different in different cases. There is then no sharp dis-

* The proposition made use of here, that "there exist at any time as many molecules, belonging to a given class, as are formed during the time of existence of a molecule (in case all molecules of that class exist for an equal time)," is often made use of in the kinetic theory. Cf. Wied. Ann. xxxiii. p. 683 (1888).

inction between a collision and the formation of a molecule ; during the time of collision the atoms form a molecule. Every collision is then an "associating" one, every molecule must exist for a certain time and then decompose of itself.

In order to bring calculation to bear on both assumptions, let us consider a new mean value of τ , namely θ , which we define in the following manner :—

$$\theta = \frac{\int_{x_0}^{x_1} \int_{y_0}^{y_1} \dots \tau \phi(x, y, \dots) dx dy \dots}{\int_{x_0}^{x_1} \int_{y_0}^{y_1} \dots \phi(x, y, \dots) dx dy \dots} \quad . . . \quad (9)$$

$$\theta = \varpi \mathfrak{S} (10)$$

Equation (10) will be found on remembering the definition of ϖ and also equation (4), and considering the condition that τ vanishes outside the limits ξ_0 and ξ_1 , η_0 and η_1 , &c. ; so that

$$\int_{x_0}^{x_1} \int_{y_0}^{y_1} \dots \tau \phi(x, y, \dots) dx dy \dots = \int_{\xi_0}^{\xi_1} \int_{\eta_0}^{\eta_1} \dots \tau \phi(x, y, \dots) dx dy \dots . . . (11)$$

From (10) it follows that

$$N_2 = Z . \theta (12)$$

According to the (β) hypothesis, $\theta = \mathfrak{S}$ and $\varpi = 1$; according to the (α) hypothesis, $\theta < \mathfrak{S}$, because in the formation of \mathfrak{S} all the molecules really formed must be taken into account ; but in that of θ every collision, associating and normal, must be reckoned ; and the latter contribute nothing to the sum of τ .

Let the mean number of impacts of an atom against other atoms be C per unit of time. If we write $CT = 1$, T is approximately the mean time which elapses between two successive collisions*. On the other hand, $Z = N_1 \frac{C}{2}$, and

* In the space v let there be N equal molecules, whose velocities are distributed according to Maxwell's law (with modulus α). If R is the smallest distance within which two molecules can approach each other without colliding, and if a molecule moving with a given velocity experiences B impacts per unit of time, the mean value of the time between successive impacts is

$$\frac{1}{B} = \frac{0.6505}{\pi} \frac{v}{NR^2\alpha} = 0.2071 \frac{v}{NR^2\alpha}$$

while

$$\frac{1}{C} = \frac{1}{B} = \frac{1}{2\sqrt{2\pi}} \frac{v}{NR^2\alpha} = 0.1995 \frac{v}{NR^2\alpha}$$

Cf. Tait, Trans. R. S. E. xxxiii. p. 74 (1886).

therefore

$$\frac{\theta}{T} = \varpi \frac{\mathfrak{S}}{T} = \frac{2N_2}{N_1} \dots \dots \dots (13)$$

According to the (α) hypothesis, \mathfrak{S} is the mean time during which the molecules exist, and T/ϖ the mean time during which a liberated atom remains free. According to the (β) hypothesis, on the other hand, θ has the former and T the latter meaning. In any case we can easily calculate θ/T or $\varpi\mathfrak{S}/T$ from this equation, since $\frac{2N_2}{N_1}$ is equal to $\frac{2(d-\delta)}{(2\delta-d)}$. For example, we have for N_2O_4 , according to the experiments quoted in § 2*,

Isotherm D. {	$p=26.80$ mm.	$\theta/T=0.096$
	(+49°·7 C.) { 497.75	1.069
Isotherm E. {	$p=49.65$ mm.	$\theta/T=0.058$
	(+73°·7 C.) { 633.27	0.396
Isotherm F. {	$p=11.73$ mm.	$\theta/T=0.016$
	(+99°·8 C.) { 732.51	0.139
Isotherm H. {	$p=35.99$ mm.	$\theta/T=0.011$
	(+129°·90 C.) { 550.29 mm.	0.023

At constant temperature we can put C proportional to $\frac{N_1}{v}$. If we write $C = \frac{N_1\psi(t)}{v}$, then $Z = \frac{N_1^2\psi(t)}{2v}$; and, according to (12),

$$N_2 = \frac{N_1^2\theta\psi(t)}{v} \dots \dots \dots (14)$$

We have thus obtained the condition (C) of § 1, but only in case θ depends on the temperature alone, and not on the pressure or volume. If we assume that the course of an impact is not affected by the frequency of occurrence of the impacts, I do not see how this condition relative to θ is to be reconciled with the hypothesis (α). In that case θ would indeed depend on the volume, in the same way that the time-interval between consecutive impacts of a molecule does. From the above table, or from Gibbs's equation, regarded as the outcome of experiment, it follows that $\varpi\mathfrak{S}/T$ varies greatly

* For nitrous acid and other dissociable gases the absolute magnitude of T is unknown. We can, however, take for granted that it is not essentially different from the length of the same time-period in such gases as oxygen, nitrogen, or nitrous oxide. We shall be within the limits when we say that the mean time of existence of the N_2O_4 molecule in the experiments quoted was somewhere between 10^{-13} and 10^{-10} second.

along any isotherm, and must in fact be proportional to $\frac{N_1}{v}$; Therefore $\varpi\mathfrak{S}$ must be constant, and consequently \mathfrak{S} also, since ϖ cannot be regarded as dependent upon v .

This conclusion can also be arrived at in the following manner. Let $\frac{N_1^2 F_1(t)}{v}$ new molecules be formed during unit

time. In unit time $\frac{N_1^2 c_1 \sqrt{t}}{v}$ collisions of two atoms take

place; therefore $F_1(t) = \varpi c_1 \sqrt{t}$, where c_1 is a constant factor. Now let us calculate how many molecules are decomposed in unit time, if hypothesis (α) be true. During unit time there take place between the molecules on the one hand, and either

molecules or atoms on the other hand, $\frac{N_2^2 c_2 \sqrt{t} + N_1 N_2 c_{12} \sqrt{t}}{v}$

collisions. Again, if ϖ_2 and ϖ_{12} denote the ratios of the number of dissociating collisions to the corresponding total number of collisions, and assuming that ϖ_2 and ϖ_{12} are independent of the volume, so that $\varpi_2 c_2 \sqrt{t} = F_2(t)$, and $\varpi_{12} c_{12} \sqrt{t} = F_{12}(t)$, the condition for equilibrium expressed in § 1 becomes

$$N_1^2 F_1(t) = N_2^2 F_2(t) + N_1 N_2 F_{12}(t),$$

which is quite different from (C) § 1.

§ 4. The equation (B) of § 1 is also, as I believe, incompatible with hypothesis (α), and for this reason, that then Maxwell's law loses its meaning. The true meaning of this law may be thus expressed:—"If two gases are mixed together, whose mean kinetic energies are different, an exchange of energy takes place until the difference disappears"*.

If two colliding atoms enter into combination, their energy divides into motion of the centre of gravity and relative motion. The molecules formed have therefore a definite mean value for the kinetic energy of the motion of the centre of gravity, which we shall call molecular motion.

Now there are two cases possible:—(i.) The molecular energy may, just after the formation of the molecule, be equal to that of the free atoms; this is the case, for example, when aggregations are formed in imperfect gases, as I have already pointed out†. Then E_1 and E_2 are equal, because this follows as a consequence of the laws of collision of atoms,

* Tait, Trans. R. S. E. xxxiii. p. 82 (1886): cf. Wied. Ann. xxxiv. p. 970 (1888).

† Wied. Ann. xxxiii. p. 687 et seq. (1888).

and not because Maxwell's law makes them equal. (ii.) The energy of the molecules formed may, on the contrary, be different from that of the free atoms, and then, according to Maxwell's law, an interchange of energy will take place between the molecules and atoms; every molecule will tend to regulate its velocity according to Maxwell's law. This phenomenon happens during the collisions of the molecule; after a few collisions the molecule will approximately fulfil the conditions of Maxwell's law. If the molecule does not last longer than the time requisite for this process of equalization of energy, or if it lasts a shorter time, the equalization can only take place in part, and only a part of the difference of energy will be equalized. A stationary condition may therefore arise, in which the ratio of the molecular and atomic energies has a value which is intermediate between unity and the value obtained from the energy of the molecules formed and that of the atoms.

Now I hope to be able to prove that the case (i.) corresponds to the hypothesis (β) of § 3, while case (ii.) corresponds to the hypothesis (α) of the same section. Let us assume that α is the most probable velocity of the atoms, so that $\frac{3}{4} m \alpha^2 = E_1$. The velocity of the progressive movement of a molecule, which is formed out of two colliding atoms, being V , let us choose V as one of the independent variables in the collision of two atoms. According to the rules laid down in § 3 of my paper "On the Kinetic Theory of Imperfect Gases" (*loc. cit.*), there will occur in unit time,

$$\frac{N_1^2 R_1^2}{v} V^2 e^{-2V^2/\alpha^2} \chi(x, y, \dots) dV dx dy \dots \quad (1)$$

collisions between atoms, in which the velocity of the centre of gravity of each lies between V and $V + dV$; and the remaining variables also lie between certain infinitely close limits, which we do not need to specify. In (1) N_1 is, as before, the number of atoms, v the volume, R_1 the characteristic distance determining whether a collision will or will not ensue between two atoms. We shall assume that in every collision of class (i.) a molecule is formed. (According to hypothesis (β) this is always the case; but on the (α) hypothesis the variables x, y, \dots must satisfy certain conditions.) There exist, then, at any time,

$$\frac{N_1^2 R_1^2}{v} \tau V^2 e^{-2V^2/\alpha^2} \chi(x, y, \dots) dV dx dy \dots \quad (2)$$

molecules of the class considered, whose duration is τ . The

mean value $\overline{V^2}$ is therefore for all molecules,

$$\overline{V^2} = \frac{\int_0^\infty \iint \dots \tau V^4 e^{-2V^2/\alpha^2} \chi(x, y, \dots) dV dx dy \dots}{\int_0^\infty \iint \dots \tau V^2 e^{-2V^2/\alpha^2} \chi(x, y, \dots) dV dx dy \dots} ; \quad (3)$$

the limits of integration with respect to x, y, \dots being $x_0, x_1; y_0, y_1; \dots$ according to the hypothesis (β), and $\xi_0, \xi_1; \eta_0, \eta_1 \dots$ on the (α) hypothesis. According to the (β) hypothesis, τ is independent of V ; but on the other assumption (α), τ depends upon the time which elapses between the collisions, and therefore on V . If we accept the (β) hypothesis as the true one, we obtain

$$\overline{V^2} = \frac{3}{4} \alpha^2 ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence

$$E_2 = m \overline{V^2} = \frac{3}{4} m \alpha^2 = E_1 . \quad . \quad . \quad . \quad . \quad (5)$$

If, on the contrary, we take the (α) hypothesis, we must write iT for τ , where T denotes the time between two successive collisions of a molecule whose velocity is V ; and $i+1$ is the number of collisions which the molecule experiences before breaking up, reckoning as first collision that in which the molecule is formed. We can treat τ as dependent on V only as T depends on V , and then i will be determined by the quantities x, y, \dots . We have then

$$\overline{V^2} = \frac{\int_0^\infty TV^4 e^{-2V^2/\alpha^2} dV}{\int_0^\infty TV^2 e^{-2V^2/\alpha^2} dV} . \quad . \quad . \quad . \quad . \quad (6)$$

Now since the relation

$$\begin{aligned} \int_0^\infty TV^4 e^{-2V^2/\alpha^2} dV &= \frac{3}{4} \alpha^2 \int_0^\infty TV^2 e^{-2V^2/\alpha^2} dV \\ &+ \frac{\alpha^2}{4} \int_0^\infty V^3 \cdot \frac{\partial T}{\partial V} e^{-2V^2/\alpha^2} dV - \frac{\alpha^2}{4} \left[TV^3 e^{-2V^2/\alpha^2} \right]_0^\infty \end{aligned}$$

holds good for all values of T , and T must be finite at $V=0$ and equal to zero at $V=\infty$ (as follows from the definition of T), we must have

$$V^2 = \frac{3}{4} \alpha^2 \left(1 + \frac{\epsilon}{3} \right) \quad \text{and} \quad E_2 = E_1 \left(1 + \frac{\epsilon}{3} \right), \quad . \quad . \quad (7)$$

in which

$$\epsilon = \frac{\int_0^\infty V^3 \frac{\partial T}{\partial V} e^{-2V^2/\alpha^2} dV}{\int_0^\infty TV^2 e^{-2V^2/\alpha^2} dV} \quad . \quad . \quad . \quad (8)$$

It will be seen that ϵ is negative, and consequently, on the hypothesis $(\alpha) \bar{V}^2 < \frac{3}{4}\alpha^2$, and $E_2 < E_1$. We shall put $E_2 = \mu E_1$ and proceed to calculate μ .

§ 5. As a first approximation we may make use of the following method. Let a molecule which moves with velocity V meet B_1 atoms and B_2 molecules during the unit of time, so that $\frac{1}{T} = B_1 + B_2$. Let us also assume that Maxwell's law holds among the molecules, the velocity-modulus being β , which is small; and that $\beta = \frac{1}{2}\mu\alpha^2$. We have then (taking the volume v equal to unity)

$$B_1 = N_1 R_{12}^2 \sqrt{\pi} \left[\alpha e^{-V^2/\alpha^2} + \frac{\alpha^2 + 2V^2}{V} \int_0^{V/\alpha} e^{-x^2} dx \right], \quad . \quad (1)$$

$$B_2 = N_2 R_2^2 \sqrt{\pi} \left[\beta e^{-V^2/\beta^2} + \frac{\beta^2 + 2V^2}{V} \int_0^{V/\beta} e^{-x^2} dx \right], \quad . \quad (2)$$

where R_{12} , R_2 are the characteristic radii for the collision of molecules with an atom or a molecule respectively. In order to calculate ϵ , let us introduce into the two integrals mean values \bar{B}_1 and \bar{B}_2 instead of the variable quantities B_1 and B_2 . As mean values we take

$$\bar{B}_1 = \frac{4}{\beta^3 \sqrt{\pi}} \int_0^\infty B_1 V^2 e^{-V^2/\beta^2} dV = 2N_1 R_{12}^2 \sqrt{\pi} (\alpha^2 + \beta^2), \quad (3)$$

$$\bar{B}_2 = \frac{4}{\beta^3 \sqrt{\pi}} \int_0^\infty B_2 V^2 e^{-V^2/\beta^2} dV = 2N_2 R_2^2 \sqrt{2\pi} \beta, \quad . \quad (4)$$

and obtain

$$\epsilon = - \frac{8 \sqrt{2} (J_1 + J_2)}{\alpha^3 \sqrt{\pi} (B_1 + B_2)}, \quad . \quad . \quad . \quad (5)$$

where

$$J_1 = N_1 R_{12}^2 \sqrt{\pi} \int_0^\infty \left[\frac{\alpha}{V} e^{-V^2/\alpha^2} + \left(2 - \frac{\alpha^2}{V^2} \right) \int_0^{V/\alpha} e^{-x^2} dx \right] V^3 e^{-2V^2/\alpha^2} dV, \quad (6)$$

$$J_2 = N_2 R_2^2 \sqrt{\pi} \int_0^\infty \left[\frac{\beta}{V} e^{-V^2/\beta^2} + \left(2 - \frac{\beta^2}{V^2} \right) \int_0^{V/\beta} e^{-x^2} dx \right] V^3 e^{-2V^2/\alpha^2} dV. \quad . \quad (7)$$

If we obtain the expression for the differential coefficient

$\frac{d}{dV} \{ V^2 e^{-2V^2/\alpha^2} F(V) \}$ and apply it to the cases $F(V) = \int_0^{V/\alpha} e^{-x^2} dx$ and $F(V) = \int_0^{V/\beta} e^{-x^2} dx$, we shall be able to calculate J_1 and J_2 easily. Their values are

$$J_1 = \frac{\pi}{8\sqrt{3}} N_1 R_{12}^2 \alpha^4; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$J_2 = \frac{\pi}{8} N_2 R_2^2 \frac{\alpha^5}{\sqrt{\alpha^2 + 2\beta^2}}; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and substituting the values of \bar{B}_1 and \bar{B}_2 from (3) and (4) in the expression (5) for ϵ ,

$$\epsilon = - \frac{N_1 R_{12}^2 + \sqrt{\frac{3}{1+\mu}} N_2 R_2^2}{\sqrt{3(2+\mu)} N_1 R_{12}^2 + \sqrt{6\mu} N_2 R_2^2}. \quad . \quad . \quad (10)$$

It follows from the definition of μ (§ 4) that $\epsilon = 3(1-\mu)$, and therefore equation (10) gives us a means of calculating the value of μ . As the general expression for μ is complicated we shall content ourselves with taking the two extreme cases. It can be shown that the minimum value of μ corresponds to $N_1=0$, the maximum value to $N_2=0$. In the first case the equation for μ is

$$18\mu(1+\mu)(1-\mu)^2 = 1;$$

and in the second case,

$$27(2+\mu)(1-\mu)^2 = 1;$$

from which the value of μ must always lie between 0.805 and 0.886.

We can check this calculation in the following manner. The probability of a molecule having a velocity between V and $V+dV$ is (from § 4) equal to

$$\frac{TV^2 e^{-2V^2/\alpha^2} dV}{\int_0^\infty TV^2 e^{-2V^2/\alpha^2} dV}. \quad . \quad . \quad . \quad . \quad (11)$$

Since $(B_1+B_2)T=1$, we have

$$\bar{B}_1 + \bar{B}_2 = \frac{\alpha^3 \sqrt{\pi}}{8\sqrt{2}J}, \quad \text{where } J = \int_0^\infty \frac{V^2 e^{-2V^2/\alpha^2}}{B_1+B_2} dV. \quad . \quad (12)$$

If we put $N_2=0$ in this equation, the value of B_1 is obtained as follows:—Let J_1 be the value of J when $N_2=0$. It is easy to show that

$$J_1 = \frac{\alpha^2}{N_1 R_{12}^2 \sqrt{\pi}} \int_0^\infty \frac{x^3 e^{-2x^2} dx}{xe^{-x^2} + (2x^2 + 1) \int_0^x e^{-x^2} dx} \quad (13)$$

In exactly the same way that Clark calculated the table given in Prof. Tait's paper previously quoted, I have found as numerical value of the integral in equation (13),

$$0.0605022.$$

Hence $\bar{B}_1 = 4.2706 N_1 R_{12}^2 \alpha$; while previously (from equation (3), putting $\mu = 0.886$ since $N_2=0$) we found for \bar{B}_1 the value $4.2584 N_1 R_{12}^2 \alpha$. In a similar manner \bar{B}_2 could be calculated. It will therefore be seen that the former method gives fairly correct results.

There is one other method of calculating μ , which I will again apply to the case $N_2=0$. From the equation (6) of § 4, we can show that

$$\bar{V}^2 = \frac{\alpha^2 \int_0^\infty \frac{V^2}{B_1} e^{-2V^2/\alpha^2} \left(3 - \frac{V}{B_1} \cdot \frac{\partial B_1}{\partial V}\right) dV}{\int_0^\infty \frac{V^2}{B_1} e^{-2V^2/\alpha^2} dV} \quad (14)$$

The denominator is equal to J_1 and is therefore known. On writing $V = \alpha x$, we obtain

$$\frac{V}{B_1} \cdot \frac{\partial B_1}{\partial V} = \frac{xe^{-x^2} + (2x^2 - 1) \int_0^x e^{-x^2} dx}{xe^{-x^2} + (2x^2 + 1) \int_0^x e^{-x^2} dx}, \quad (15)$$

whence

$$V^2 = \frac{\alpha^2}{2J_1} \int_0^\infty \frac{x^3 e^{-2x^2}}{xe^{-x^2} + (2x^2 + 1) \int_0^x e^{-x^2} dx} \left[1 + \frac{\int_0^x e^{-x^2} dx}{xe^{-x^2} + (2x^2 + 1) \int_0^x e^{-x^2} dx}\right] dx. \quad (16)$$

Applying Clark's method, I have found for the numerical value of the integral (16), 0.088139, which gives

$$\bar{V}^2 = 0.67776 \alpha^2.$$

The previous calculation, with $\mu=0.886$, gave the value

$$\overline{V^2} = \frac{3\mu}{4} \alpha^2 = 0.66450 \alpha^2.$$

This calculation can also be extended to the case $N_1=0$, and I have worked it out for that case. We may conclude that if μ represents the ratio of the energy of the molecules formed to the atomic energy, the value of μ always lies between $\frac{4}{9}$ and $\frac{8}{9}$; and the final ratio of the two energies, which remains stationary, lies between μ and 1.

§ 6. The problem dealt with above appears to me to be of great interest in the theory of dissociation. If the mean values of the kinetic energies of a molecule and an atom are different, and do not even stand in a constant ratio to each other, it is difficult to decide which mean value should be taken as a measure of the temperature. As previously in the case of imperfect gases*, so also here it is seen that in the kinetic theory of heat we are far from possessing a general definition of temperature; the usual one is applicable only to perfect gases.

§ 7. Now since the hypothesis (α) appears to be at variance with experiment in actual dissociation phenomena (dissociation of iodine vapour, nitrous acid, &c.), and would only be applicable to phenomena of decomposition, which are due to secondary causes (*e. g.* the dissociation of hydriodic acid), it would be necessary to suppose that iodine atoms, NO_2 groups, &c., only combine into molecules during collision. Since all gases may probably dissociate under suitable circumstances, this assumption would have to be extended universally to all gaseous molecules. We should then have to make, for gases like oxygen, hydrogen, &c., the further supposition that θ/T is very large and nearly constant, or else free atoms would occur in impossible numbers in these gases. According to experiments hitherto made on atomic weights and densities of gases, it must be assumed that in these cases θ is far greater than 500 T.

* L. Natanson, Wied. *Ann.* xxxiii. p. 693 (1888). I have formerly tried to prove that the energy of the "free" molecules should be taken as a measure of the temperature. In a paper which I know only by an abstract (*Proc. R. S. E.* xvi. p. 69, 1889), Tait arrives at the same conclusion by quite another line of argument.

III. *The Temperature of the Moon.* From *Studies at the Allegheny Observatory* by S. P. LANGLEY, with the assistance of F. W. VERY*.

THIS memoir may be regarded as the completion of the investigation commenced in 1883, and continued during the next four years, and of which previous portions have been published in the *Memoirs of the National Academy of Sciences*, in a paper read Oct. 17, 1884 (vol. iii.), and in that read Nov. 9, 1886 (vol. iv.), the latter having been published in abstract in the *American Journal of Science*†.

The original memoir, of which the following is a very succinct abstract, can, from its special character, hardly claim the attention of the general reader; but the latter may, perhaps, be here reminded that the main questions at issue are the temperature of an airless planet at the earth's distance from the sun, the action of the atmosphere in modifying the temperature of such a planet, and, in general, the study of those conditions of radiation and absorption which have actually rendered life possible on our own. He may be reminded also that it has been generally assumed hitherto that the temperature of the sunlit surface of an airless planet at such a distance, *e. g.* of the moon, would be excessively high. Thus Sir John Herschel, in his latest '*Outlines of Astronomy*,' says:—"The surface of the full moon exposed to us must necessarily be very much heated, *possibly* to a degree much exceeding that of boiling water." The only experimental evidence obtainable appeared to lend support to this view, for though Lord Rosse did not undertake to directly determine the lunar temperature (as he is often supposed to have done), any inference which can be drawn from his experiments appears to support the above views of Herschel, which he also cites‡.

It has also been almost universally supposed that our atmosphere was nearly impervious to the lunar radiant heat, so that, if any existed, it could still not be perceived by us at

* Memoir read to the National Academy of Sciences, November 1887. Communicated by the Author.

† For December 1888. See also '*London, Edinburgh, and Dublin Philosophical Magazine*,' December 1888; also *Ann. de Chimie et de Physique*, July 1889.

‡ See *Proc. Royal Society*, xvii. 1869, p. 443; xix. 1870, p. 12; *Transactions*, clxiii. pp. 622-4. Having elsewhere shown that the lunar radiation consists of a small quantity of reflected heat and a comparatively large quantity of heat emitted from its soil, Lord Rosse compares

the sea-level. Thus Sir John Herschel says of the moon that "its heat (conformably to what is observed of that of bodies heated below the point of luminosity) is much more readily absorbed in traversing transparent media than direct solar heat, and is extinguished in the upper regions of the atmosphere, never reaching the surface of the earth at all."

The reader may also be reminded that these statements have remained unchallenged on account of the hitherto insuperable difficulties of experimental investigation, arising from the all but infinitesimal amount of heat which the moon sends us, and the added fact that this heat, small as it is, is necessarily of two essentially different kinds—that which the moon, acting as a mirror, reflects from the sun, and that which directly emanates from the substance of her own sun-heated soil, while it is only by an analysis of each of these two kinds of heat, each in its totality non-existent to the most sensitive thermometer, that we can expect to give an experimental answer to the question*.

It was Melloni who, on Mt. Vesuvius in 1846, by the employment of a polyzonal lens, one metre in diameter, and the newly invented thermopile and galvanometer, first succeeded in getting *any* certain indications of heat from the moon, though these were of the feeblest kind. It is Lord Rosse, employing the Parsonstown telescope with improved thermopiles and galvanometers, who has the credit of abundantly confirming Melloni's observation of the fact of the moon's radiant heat being perceptible, and further the great merit of making a preliminary investigation of its character, by showing by its imperfect passage through glass that it is chiefly non-reflected heat. Lord Rosse, however, as has been

the total excess of this lunar radiation over that from the sky by means of that from two blackened vessels, one producing the same effect on his thermopile and galvanometer as the sky, the other as the moon, and finds that the observed galvanometer range is that due to a temperature of excess in the latter vessel, to be computed at $197^{\circ}5$ F. if Dulong and Petit's law of cooling is used, or at a still higher one if Newton's is employed. The effective sky temperature was about $+20^{\circ}$ F., so that if we suppose the result due wholly (instead of mainly) to the emitted heat, this would indicate a temperature of the lunar soil at any rate above that of boiling water. Lord Rosse, however, in view of the empirical character of the formula employed and of other considerations, is careful to state as his conclusion "that the problem of the determination of the lunar temperature is nearly as far as ever removed from our grasp."

* In an appendix (No. 1) of the memoir referred to, will be found a historical account, believed to be fairly complete, of the labours of previous thinkers and workers in this subject.

said, concludes that the problem of the moon's temperature is still indeterminate.

At this point the question is taken up by the writer, who, with the aid of the bolometer, used directly in the lunar image, had already reached, in the first of the memoirs mentioned above, the following inference among others of less importance, viz. *that the sunlit surface of the moon is not far from the freezing temperature.*

This inference resulted both from observations in the direct beam and from a preliminary and partially successful attempt to form a heat spectrum, for this gave indications of *two* maxima in the heat-curve—the first corresponding to the heat from the solar reflected rays; the second (indefinitely lower down in the spectrum) corresponding to a greater amount of radiant heat emitted from a source at a far lower temperature, lower at any rate than that of boiling water, above which the temperature of the lunar soil has been hitherto supposed to not improbably be. This statement of the first memoir is put forward as inferential and probable merely, and not as conclusively proven.

The second memoir, on “The Solar and the Lunar Spectrum,” is chiefly devoted to the invisible spectrum of the sun, but incidentally describes the progress in the improvement of the apparatus employed so as to better fit it for the delicate task,

(1) of measuring the already feeble lunar heat when diffused by expansion into a lunar spectrum; and

(2) of determining the possible existence and the exact position of the two heat maxima already described in the first memoir.

We are now prepared to take up the present memoir, and give an abstract of its results. It contains researches pursued through several years with constantly improving instrumental means, and while the writer cannot feel that (owing to the extreme experimental difficulty of the subject) the results have obtained a certitude corresponding to the great labour bestowed upon them, he believes that this labour is justified by the fact that it has not been given to a question of merely abstract interest, but that the whole subjects of terrestrial radiation and the conditions of organic life upon our planet are intimately related to the present research.

Spectroscopy has hitherto dealt almost exclusively with
Phil. Mag. S. 5. Vol. 29. No. 176. Jan. 1890. D

light, but in this new field we consider chiefly that great invisible spectral region in which the *entire* radiation of the soil of our own planet is to be found, a region of which we have, until quite recently, known nothing. To see how the question of the lunar heat affects our knowledge on the whole subject of our planet's temperature, we must remember that, until a few years past, it had been assumed by all writers of repute that the earth's atmosphere acted exactly like the glass cover of a hot-bed, and kept the planet warm in exactly the same way that the hot-bed is warmed, by admitting the light-heat of the sun, which was returned by the soil in the invisible radiation of greater wave-length to which the atmosphere was supposed to be impervious, and that thus the heat was stored, glass being till lately supposed to be practically athermanous to *all* infra-red heat. It was a necessary part of this assumption that all, or very nearly all, the infra-red was absorbed by our atmosphere; but in 1881, the observations of the Mount Whitney expedition, supplementing previous ones made at this observatory, showed that through the infra-red, *as far as it had then been explored*, the atmosphere transmitted the invisible rays with greater facility even than the luminous heat; so that the ordinarily received idea must be essentially modified, and, if the absorption of the telluric radiation did indeed take place as supposed, it must be in spectral regions then entirely unknown. It is in an examination of these, till now, quite unknown regions beyond the extreme boundaries of former researches on the infra-red, and in the study of the radiations of corresponding wave-length emitted from the lunar soil, that we find the principal subject-matter of the present memoir*.

It is, in introduction, again pointed out that the absorption of the earth's atmosphere for these radiations, as for all others, is not simple, but eminently complex, and that the old formulæ lead to gross errors in practice. Further, as the amount of radiation of a planet is, like that of any other body, dependent on that of its surroundings, reasons are repeated for believing that the so-called temperature of space (a term due to Fourier and afterwards adopted by Pouillet, who fixed its

* The reader is reminded that the words "infra-red" have obtained an extension of meaning, since we have been able to show in previous memoirs, not only the vast amount of the energy in this region (which, in the case of the sun, is over 100 times that in the ultra-violet), but that in this invisible infra-red there is every variety of condition, greater differences than there are *e. g.* between violet and orange light, and that Melloni's anticipatory comparison of varieties of radiant heat to varieties of colour actually understates the truth.

value at -142° Cent.) has no sensible existence, but may be here treated as that of the absolute zero.

There is next given a description of the apparatus, which consists essentially of a siderostat, carrying an 18-inch mirror, and capable of sending a lunar beam of corresponding capacity horizontally into an adjoining dark room and keeping it fixed there during the night's observations. In the path of the beam can be interposed a large double screen of blackened copper, ordinarily filled with water. The beam then falls on a condensing mirror, whose ordinary aperture of 8 inches does not, as may be seen, utilize the whole of the beam transmitted by the siderostat, but has been selected in reference to the capacity of the rock-salt train of lenses and prisms which forms the spectrum. This train is believed to consist of pieces of salt of hitherto unapproached perfection in workmanship, as at the time our investigation commenced no salt prisms were procurable giving a single Fraunhofer line in the solar spectrum; while with the actual rock-salt train, D is divided in the spectrum of the moon. The general construction of the spectrobolometer, and of the special bolometer employed with it, will be found given in previous papers*.

There are three principal methods of investigation:—

First, the measurement of the total heat of the moon with a concave mirror, admitting the interposition of a sheet of glass to rudely indicate the quality of lunar rays as compared with those of the sun. This method, which was that employed by Lord Rosse, has been very thoroughly practised here with results which have been partly given in the previous memoir.

Second, a method, practised here for the first time, and yielding quite peculiar results, has been to form, usually with this same mirror, an image of the moon, but to now let this fall upon the slit of a special spectroscope provided with the rock-salt train referred to; and after expanding this excessively minute heat in this way, it has been found possible, with late improvements in the apparatus, to measure by the bolometer the different degrees of heat in the different parts of this lunar heat-spectrum, both visible and invisible. The doing of this, with its results, forms the principal subject of the present memoir.

Third, since such a mirror as that just mentioned, owing to its short focus, forms an extremely small lunar image, in certain observations (carried on, however, only during a limited

* See this Journal, xv. March 1883, and xxi. May 1886. For a description of the improved form of bolometer and galvanometer see vol. xxii. August 1886.

time), we have taken advantage of the sensitiveness of our apparatus to directly explore a large lunar image with the bolometer, in spite of the diminished heat in such a one. For this purpose a special mirror, 303 millim. in diameter and 3137 millim. focus, giving a lunar image of about 30 millim. diameter, has been employed. On the occasion of a lunar eclipse the last-named apparatus has also been used.

We have already alluded (see *Memoirs of the National Academy*, vol. iii. p. 20) to the especial importance of the action of the screen in these observations. This arises from the fact, as will be seen later, that we shall deal with lunar heat of a totally different quality from that of moonlight or sunlight. It is, in a large part, radiation emanating from the lunar soil, and of a quality, as we shall see, approximating to that of the screen itself. It must be evident, then, that the radiations from this screen assume here a wholly abnormal importance.

An investigation of the theory of the screen accordingly occupies a chapter, for which the reader is referred to the original. We may remark here, in passing, that the investigation incidentally offers an explanation of the empirically known fact, that the velocity of cooling of a hot body at various temperatures of excess varies with that of the enclosure itself. The discussion also indicates what appears to be an independent method of determining the absolute zero; but the method, although apparently correct in theory, would demand observations more accurate than our own casual ones to give it practical value. It may be, however, worth mentioning that the observations, such as they are, indicate by this novel method the existence of an absolute zero at a point between -250° and -300° Cent.

A list of all the observations in the lunar spectrum extending from October 1884 to February 1887 is then given, together with some collateral ones upon the "great radiator." This latter instrument may be briefly described as analogous to an immense Leslie cube, presenting as it does a blackened radiating surface at the temperature of boiling water and of 1 square metre area. The object in giving it this extraordinary dimension is to enable it to still angularly subtend the whole field of view of the bolometer, while it is at such a distance that the intervening column of air may be supposed to exercise a measurable absorptive effect. Its actual distance was 100 metres, and at this distance the absorption of the intervening air on the dark radiant heat, emanating from its surface at 100° Cent., was in fact manifest, and gave evidence, novel and interesting, both as to the actual absorption by our

atmosphere for radiations from bodies of low temperature, and as to the spectral region where it chiefly occurred.

This list includes, besides the described heat observations on the moon at every obtainable lunation, the following others:—

- (1) On the heat during a lunar eclipse.
- (2) On the quality of the heat in the lunar spectrum at different stages of the moon's age.
- (3) On the direct heat observable from different regions of the moon's face in an enlarged lunar image, and comparisons of the heat radiated by the dark and by the bright regions of the moon.
- (4) A supplementary investigation showing that different percentages of the radiations from these dark and bright regions were transmitted by glass.
- (5) Observations giving the means of comparing the atmospheric absorption of lunar radiations in summer with that in winter for equal altitudes.
- (6) Very numerous observations of the spectrum of the midnight sky.

(These last are specially important here, where they are rendered necessary by the fact that this sky is the standard with which the lunar radiations are to be compared. These last observations give, for example, certain evidence of a great "hot band" in the negative sky spectrum, corresponding in position to the great cold band in the lunar spectrum, which is thus shown to be produced jointly by the absorption of the moon's rays and by the absorption of the radiation of the bolometer due to the intervening air-column between it and the moon.)

- (7) Observations supplementary to the last, by comparative measurements of the sky radiation from the zenith to the horizon.
- (8) On further supplementary measurements made by comparing the energy in the spectrum of a lampblack screen at 100° C. with that of the sky, showing the existence of several regions of atmospheric absorption, giving "hot bands" in the negative sky spectrum.

(We only allude here, in passing, to the important inference to be drawn with regard to the nocturnal radiations from the soil of our own planet, to which these observations show that our atmosphere is partially diathermanous.)

(9) On other measurements giving the means of estimating the total lunar radiation in terms of solar ; but for these and many more subsidiary ones, the reader must again be referred to the original memoir.

The only one of these subsidiary researches which needs further mention here is the measurement of the heat from different parts of the *eclipsed* moon, on the night of September 23, 1885.

The diameter of the lunar image was 28·3 millim., and of this only a limited portion (0·08 of the whole) fell upon the bolometer. As the penumbra came on, the diminution of heat was marked, being measured by the bolometer even before the eye had detected any appearance of shadow. The heat continued to diminish rapidly with the progress of the immersion in the penumbra, but at no time did the lunar radiation from the part in full shadow entirely vanish. At one hour before the middle of the total eclipse, the deflexion in the umbra was 3·8 divisions. Fifty minutes after the middle of the eclipse it had diminished to approximately 1·3 divisions, less than one per cent. of the heat from a similar portion of the uneclipsed moon, a deflexion so small that its significance may be somewhat doubtful. It need hardly be stated that this heat from the eclipsed moon was almost absolutely cut off by the interposition of glass. The rise of the temperature after the passage of the umbra was apparently nearly as rapid as the previous fall. The vicissitudes of the lunar climate indicated by these observations in the short time of a few hours, must exceed the change from our torrid zone to the greatest cold of an arctic winter.

In this connexion it should be stated that repeated observations on the dark side of the moon have given only the same heat-spectrum as shown by the sky away from the moon, the conclusion being that, so far as our present observation carries us, the moon has no internal heat sensible at the surface, so that the radiations from the lunar soil, already spoken of, are to be understood as due purely to solar heat which has been absorbed and almost immediately re-radiated.

The principal method employed in the present research for determining the temperature of the surface of the moon is founded on the fact, already experimentally established by the writer, that the position of the maximum in a curve, representing invisible radiant heat, furnishes a reliable criterion as to the temperature of the radiating (solid) body *,

* Proc. Am. Assoc. for Adv. of Sci., 1885; also Phil. Mag. xxi. May 1886.

and on the further fact, established by Mr. F. W. Very and the writer, that two distinct heat-maxima are observable in the lunar spectrum, one corresponding to the radiation reflected from the soil, the other to that emitted by it. It at first seemed, in accordance with what has just been said, that the accurate determination of the wave-length of this latter maximum would give a correspondingly accurate determination of the temperature of the sunlit surface of the moon; and, accordingly, to this object the main portion of the observations were given. We may anticipate what follows by here saying that by this method, a perfectly correct one in theory, the writer believes that the temperature of the lunar soil could be determined with great exactness, were it not for the intervention of the earth's atmosphere, which exercises, in this part of the spectrum as in every other, a highly selective absorption, indicated here, however, not by fine lines like the Fraunhofer lines of the solar spectrum, but by enormously wide "cold bands," which vary in size and even in position from night to night*, rendering the exact position of this maximum in a corresponding degree indeterminate.

Another chapter is occupied by an example of a single night's work in detail, with a statement of some of the precautions and corrections employed in practice. It may be observed here in general as to the apparatus, that while the rock-salt train, as already mentioned, is of such perfection as to show the Fraunhofer lines very completely in the lunar luminous spectrum, the accompanying bolometer and galvanometer enable us to measure cold bands in the non-luminous lunar or air spectrum, whose heat is otherwise so inappreciably small that it corresponds to a radiation of $\frac{1}{100000000}$ of a caloric per second, measured by the generation of a current of 0.000,000,001 ampere. This is the amount of heat and current implied in moving the galvanometer image over 1 millim. of the scale. In fact, the image is quite steady enough under favourable conditions to admit of the observation of less heat than this, giving deflexions of fractional portions of a millimetre; but owing to fluctuations in the absorption of our atmosphere which transmits this radiation, rather than to any limitations of the instrument itself,

* That an absorption-band may vary in magnitude will excite no surprise, but that it should vary sensibly in position may appear to some in contradiction with our knowledge of the fixity of lines in the upper spectrum. An explanation of the anomaly will be found in this Journal for Dec. 1888.

it is generally found best not to note deflexions of less than 1 millim. What has just been said refers particularly to measurements of the diffused heat from the moon's soil in the invisible lunar spectrum and to the corresponding spectral analysis of the reflected heat. When, however, we place the bolometer directly in the lunar image formed by the 8-inch aperture, the deflexion throws the needle at once off the scale, and is found on more careful measurement to correspond under favourable circumstances to a potential deflexion of about 1500 millim. divisions. Melloni, it will be remembered, obtained four or five divisions on his galvanometer with the thermopile and the metre polyzonal lens on Vesuvius, and the immense difference just noted is some indication of the advance of experimental physics in this matter since his day.

*Theory of Observation ; with typical example,
showing Method.*

Every observation on the moon, whether on its total heat, as observed directly in the lunar image, or on its diffused heat in the spectrum, should consist in a comparison of its radiations with those of the adjacent sky on either side of it. If our thermometric apparatus had an absolute scale, and there were no intervening atmosphere, it appears, in accordance with what has already been said, that such apparatus, when directed not to the moon but to "space" more or less adjacent, should indicate the temperature of this space, which is sensibly that of the absolute zero; and then, when it is turned upon the moon, supposing it to receive only the emitted and not the reflected heat, it would give, also on the absolute scale, the temperature of the lunar soil. In fact, with such an absolute thermometer, the preliminary comparison with space would be unnecessary. In reality, we use not an absolute apparatus with a natural scale, but a differential apparatus with an arbitrary scale; and if we could work without an intervening atmosphere, we should, even in this case, require to let the bolometer radiate to space in order to determine the point on our arbitrary scale which corresponds to zero. We should then observe a second point corresponding to the temperature of the lunar surface, and having determined the value of the units of our arbitrary scale in terms of the natural one, we should evidently have the quantity sought.

The above conditions are still of ideal simplicity. The great, the almost insuperable difficulty of actual observation, lies less in the minuteness of the actual radiation, or even in its two-fold character, than in the fact that it is masked to us by the changes of an always intervening atmosphere. The case of observations on the sun is totally different from the present one, and would be so even if the sun were withdrawn till it emitted no more heat than the moon; for in this latter imaginary case, the greater portion of the solar radiation would still lie in a spectral region totally distinct from that in which the radiations proper to the obscuring atmosphere are found, and it is the peculiar, unavoidable difficulty, at every stage of this long investigation, that since the moon and the air are both alike cold bodies, their invisible spectra are, in general, superposed in the same field. Let us add to this, that the (invisible) spectrum of the air is usually not fixed but fluctuating, and we shall see the desirability of having some separate standard with which to compare it from night to night. This we obtain most conveniently by filling a vessel of proper shape and size, either with water or with a freezing mixture at a temperature constant for the series, and making this vessel itself the screen which is interposed between the bolometer and the lunar rays. The bolometer must remain unmoved, and the direction of the heat-receiving apparatus to the east or west of the moon must always be understood to be obtained by a slight motion of the siderostat mirror.

That the minute change in the angle of presentation of the face of this mirror does not affect its own radiations appreciably might well be anticipated, but is a fact which has not been left unproven by direct experiment. The bolometer, then, enclosed in a non-conducting case which cuts off radiations from every object but the mirror or prism immediately in front of it, practically feels only the radiations from the moon, or from the sky immediately on each side of it, except when the screen is interposed. Mirrors and prisms do indeed radiate heat to it from their own substance, but these radiations may be considered as absolutely constant, and as therefore absolutely negligible during the brief cycle of a single observation.

We confine ourselves here to the above general explanation, referring the reader who may be interested in the details of the observations to the original memoir, remarking, however, that the actual spectral position of a ray is given by a circle, reading to $10''$ of arc, and that previous measures of our

own* enable us to convert this arc into wave-length. This fixes the position of bands in the spectrum. The amount of heat in any portion of the spectrum is, within the narrow limits of errors of observation, strictly proportional to the deflexion on the galvanometer-scale (the conditions of the bolometer, battery-current, galvanometer, &c., remaining constant). As these degrees are arbitrary, they are converted into thermometric degrees by a process fully detailed in the original memoir.

The preliminary record of the humidity, state of the sky, temperature, &c., is nearly self-explanatory. We need only explain that "Rock-salt lenses at 37 centim." refers to the fact that the focal length of these lenses increases from 35 centim. in the visible spectrum to one indefinitely greater with heat of great wave-length, and that this focus accordingly needs to be adjusted for the particular part of the heat-spectrum under study.

"Deflexion per degree Centigrade" refers to the use of a constant determined for each evening, giving the actual deflexion the galvanometer produces, for each degree of excess of temperature in a certain standard Leslie cube at a certain standard distance from the bolometer.

The order of observation consists first in noting the time. (We will suppose, in the example which follows, that the time is 9^h·08 M. T., on the evening of February 9, 1887); next, in noting the prismatic deviation corresponding to the actual position of the bolometer in the spectrum, which in this particular case is 41° 08' 30", or that of the D line in the visible spectrum. Previously to observation the bolometer has been radiating through the spectroscopic train and mirror to the special screen described, which, on this particular evening, is at the constant temperature of + 18° Cent. Under these circumstances, the needle will take up some position representing radiation to the screen, which at this first exposure we will call A, its position here on our arbitrary scale being at the 215th millimetre. During this time the siderostat-mirror has been so placed as to be sending towards the bolometer radiations from the sky on the *east* of the moon†. Call the effect of these particular sky radiations B. They have been intercepted by the screen, but now the screen is withdrawn, and the bolometer radiating to this eastern adjacent sky receives less heat than the screen

* See Phil. Mag. xxii. August 1886.

† The area of sky observed is virtually the same as that of the moon.

gave it (213.2). The siderostat-mirror is moved to throw on the image of the moon. Let us call the resultant deflexion C. The moon appears in this example very slightly warmer than the sky, for the image moves on to 213.4. Next, by another adjustment of the siderostat-mirror, the sky *west* of moon is thrown on. Call this result D. The image on the galvanometer-scale moves back to 211.9, indicating cold. Finally the screen is interposed the second time. Call this second interposition E. In an ideally constant apparatus, the second interposition of the screen should give the same reading as the first. Actually 210 divisions is obtained, instead of 215 as before, owing to the so-called "drift" of the needle during observation. The mean of the two readings for sky-east and sky-west is now subtracted from that for the

moon and gives, under the column $C - \frac{B+D}{2}$, the difference

between the temperature of the moon and the sky in our arbitrary degrees. It will be seen from a comparison of all the numbers in this column that there are fairly accordant indications of a maximum near the prismatic deviation of $39^{\circ} 30'$, which corresponds with the wave-length of $2^{\mu}.1$, and approximately with the maximum of the solar-heat curve. There is another maximum of far greater magnitude near $37^{\circ} 30'$ (wave-length about 14^{μ}), corresponding to the maximum known to exist in the radiations of bodies at a temperature of about 0° Cent., and due, it would seem almost beyond doubt, to radiations from the sun-heated lunar soil. It will be seen also that all numbers in this column have one sign, *i. e.* the positive, indicating that throughout this series, without exception, the moon has been found warmer than the adjacent sky. This, indeed, is to be expected, since, without the atmosphere, the temperature of this sky would be nearly that of the absolute zero, and at any rate lower than that of the moon. The difference is so considerable that even the temperature fluctuations due to the interposition of the intervening atmosphere in no case this evening hide the fact.

In order to compare the fluctuating radiation of the atmosphere with a constant source, we take the mean of the sky observations and compare it with the mean of the readings on

the screen. In this particular case, $\frac{B+D}{2} - \frac{A+E}{2}$ gives a dif-

ference of but 0.1 division; but this is, as we have already observed, when the bolometer is directed towards the orange

in the luminous part of the spectrum, and our cold screen, it need hardly be said, is not emitting any rays of orange light. We conclude, then, that the apparent deflexion of 0.1 div. here has no real significance; but, as we go down the spectrum towards the region of the radiation from cold bodies, we find, beyond deviation 39° ($\lambda = 4^{\mu}3$), values which indicate a real excess of screen over sky radiations.

We have selected the first number in our second series of Feb. 9, 1887, as the example, because this follows the normal course without marked instrumental disturbance. The nature of these fortuitous disturbances and the methods adopted for their correction are explained in the original memoir. In many cases, as will be seen, they may cause the sky on one side or the other of the moon to appear momentarily warmer, although the mean of the two is colder.

Comparisons of the sky and screen by directing the bolometer to the sky at the zenith and at the east and west horizons follow, and three double series at the most important points in the spectrum, made with the moon at a high, a low, and an intermediate altitude, give indications of the atmospheric absorption. These, however, are not given here, but only the double series (No. 2), of which a literal transcript from the book of original entry now follows:—

Station, Allegheny.

Date, February 9, 1887.

Wet bulb at 7h 30m = $+11^{\circ}2$ C. } Internal.
Dry bulb at 7h 30m = $+16^{\circ}0$ C. }

Temperature apparatus at 9h 45m = $+19^{\circ}8$ C.

External temperature, near the freezing-point.

State of sky at 8h 30m clear. Very good sky.

Aperture of slit = 3 millim. = $27'9$.

Prism used L_{11} ; $\Lambda = 60^{\circ}00'28''$.

Rock-salt lenses set at 37 centim.

Spectrum thrown west.

Galvanometer No. 3.

Time single vibration = 12 sec.

Deflexion per degree Centigrade = 17.8.

Bolometer No. 1; aperture = 3 millim. = $27'9$.

Setting on $D_2 = 41^{\circ}08'30''$.

Battery current = 0.036 ampere.

Reader at circle, J. P.

Reader at galvanometer, F. W. V.

Time.	Devia- tion.	Screen A.	Sky B.	Moon C.	Sky D.	Screen E.	$C - \frac{B+D}{2}$	$\frac{B+D}{2} - \frac{A+E}{2}$
Series II.								
h m								
9 08	41 08 30	215	213.2	213.4	211.9	210	0.8	+0.1
	40 20	228	233	235.6	234.8	233.8	1.7	+3.0
	40 00	183.8	183	184.6	181	180	2.6	+0.1
	39 40	183.8	185	188.2	184.2	184	3.6	+0.7
	20	192	193.5	198.8	196	197	4.1	+0.2
	39 00	185	185.3	188.4	186	188	2.7	-0.8
9 20	38 40	197.7	196.2	198.3	197.5	197.8	1.5	-0.9
	30	214	213	214.5	212	212.8	2.0	-0.9
	20	182.5	183	183.6	182.4	184	0.9	-0.6
	10	185	184.6	186.7	186.7	189	1.0	-1.0
	38 00	191.6	184	189.2	182.8	186.2	5.8	-5.5
	37 50	175	170.8	180	167	170.2	11.1	-3.7
	40	167.4	161	177.2	159.4	168	17.0	-7.5
	30	171.4	165	181.8	161.2	172	18.7	-8.6
	20	171	166.7	182.8	164	171.7	17.4	-5.9
	10	173	169	182	168.8	176.2	13.1	-5.7
	37 00	173	166.5	176	166	174	9.7	-7.5
	36 00	178.2	174	184	172.8	178.2	10.6	-4.8
9 42	35 00	183.2	182	184.3	179.6	180.6	3.5	-1.1

Temperature of Screen = 18°.

9 45	35 00	190	185	186.2	178.2	181	4.6	-3.9
	36 00	191	190	201.3	191.8	197.6	10.4	-3.4
	37 00	199.5	193.8	205.5	192.2	200.9	12.5	-7.2
	10	198.2	190	203	186.8	195	14.6	-8.2
	20	189.5	181.5	197.2	178	187.1	17.5	-8.6
	30	188.2	182.4	200.2	180	189.5	19.0	-7.9
	40	189	183.5	200.5	178	182	19.4	-4.4
	50	181.4	176.3	188.8	175.4	176	12.8	-2.7
	38 00	173.6	172.8	180.6	175.9	181	6.3	-3.0
10 00	10	185	183.7	185.8	185	1.8	1.4	-2.1
	20	195	195.9	198	197.8	199.7	1.2	-0.6
	30	203	203.5	205	201	201	2.8	+0.2
	40	209.7	208	208.7	206	205.8	1.7	-0.7
	39 00	206	207	211.2	207.4	209	4.0	-0.3
	20	210	211.4	215	210.5	210.5	4.0	+0.7
	40	200.5	201.5	205	201	202.3	3.7	-0.1
	40 00	206.4	209.2	215	211.6	211.6	4.8	+1.2
	20	214.5	214.7	217	214	215	2.7	-0.4
10 20	41 08 30	221.4	222	224.1	223.2	223	1.5	+0.4

The observations of this night may serve as a type of a great many others. They all show *two* maxima (see column $C - \frac{B+D}{2}$) whose apparent position differs little from that already given in the example, and it may be added that in all cases the radically different character of the heat in these two maxima bears the proof of the independent test furnished by

passing the rays through glass before measurement, the rays from the upper maximum passing freely, as rays belonging to the maximum of solar reflected heat should do; those in the lower maximum, on the contrary, being absolutely cut off by the glass, as rays of this wave-length from a source at a temperature below that of boiling water are known to be. This test of the glass employed by Lord Rosse in the direct lunar beam, is here, it will be observed, applied at different parts of the lunar heat-spectrum; and its result in the latter case, corroborating that already obtained by the respective wave-lengths of the maxima, brings evidence of a radiation of heat from the lunar soil at a temperature at any rate below that of boiling water.

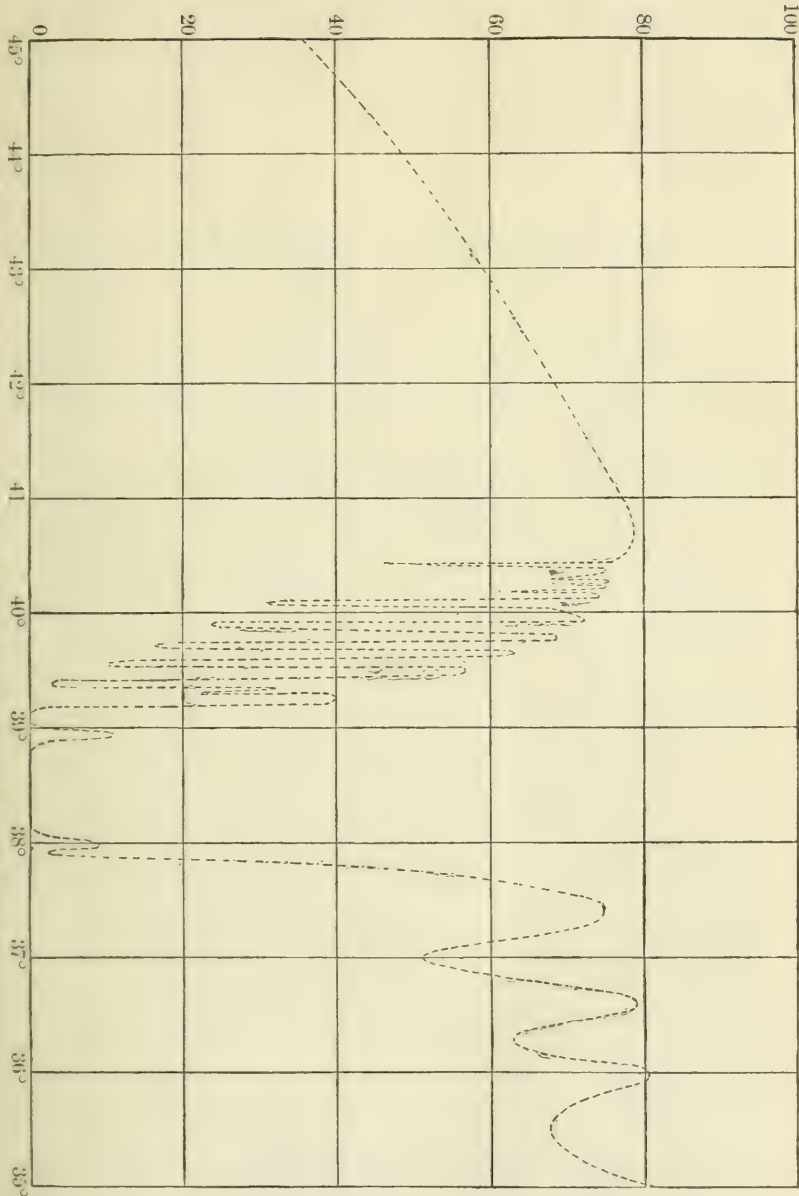
Other observations furnish the means of computing the relative absorption of the earth's atmosphere as exhibited in extended cold bands in the region of the lower maximum. Then, from a combination of the two, we are enabled to reach a certain approximation to the position and magnitude of this maximum as it would appear if the atmosphere had not intervened. The existence of some of the principal atmospheric cold bands in this region, due to the absorption exercised by an atmospheric column 100 metres in length, has been quite independently determined by means of the great radiator already referred to. During moist summer weather two principal maxima have been found in its spectrum—the larger at deviation $37^{\circ} 15'$, nearly agreeing with the lunar curve in summer, a second smaller maximum at deviation $38^{\circ} 45'$, and between them a cold band with its minimum at deviation $38^{\circ} 20'$. Remembering that the unabsorbed spectrum from a radiating surface of lampblack, at the temperature of boiling water, has its maximum at $38^{\circ} 25'$, or very near the deepest depression of the cold band, it will be recognized that we have evidence of a considerable absorption at this point.

To this must be added the fact, shown by our observations, that in the case of solids the greater part of the whole heat is always found *below* the maximum of the (unabsorbed) prismatic curve. If this law hold in the case of the sun, since little heat is found below its actual prismatic maximum (near deviation $39^{\circ} 40'$), the inference is that absorption in that region (*i. e.* the *extreme* infra-red), must have been great.

Arguments on these different lines, combined with another derived from a direct comparison of sun and electric-arc radiation, which will be described farther on, enable us to present a curve (fig. 1) showing, with the degree of approximation compatible to the first attempt in such a field, the atmospheric absorption in all parts of the spectrum.

Per cent.

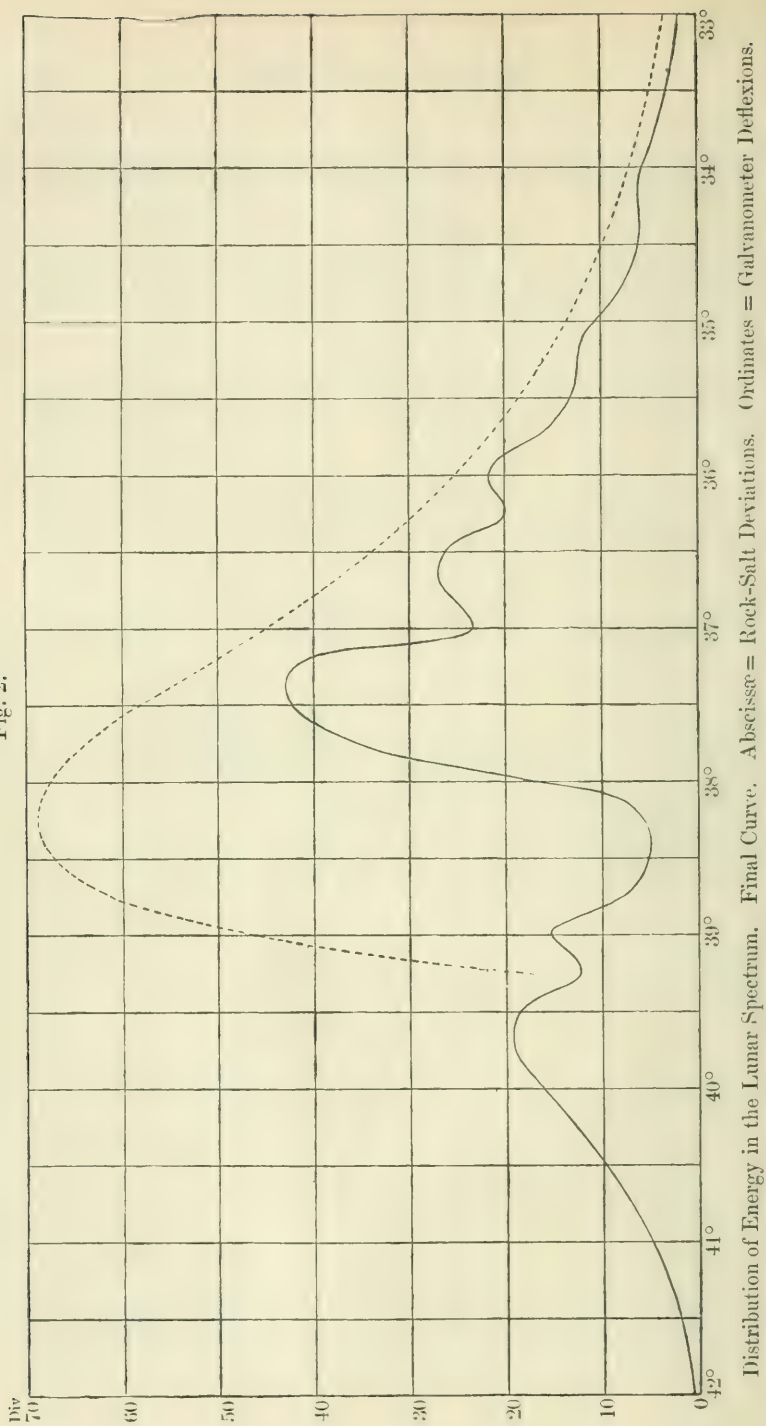
Fig. 1.



Transmission of Radiation by the Earth's Atmosphere. Abscissæ = Rock-Salt Deviations.

Ordinates = Percentage of Transmission.

Fig. 2.



The final result of the measurements, extending over the three years from 1884 to 1887, is given in fig. 2, in which abscissæ correspond to deviations of a rock-salt prism of 60° , vertical ordinates to directly observed heat from radiations, while the dotted curve indicates what seems to be the most probable position and amount of the lower maximum, as it would be observed were there no intervening atmosphere. The following remarks may serve to make the full meaning of this curve clearer.

The heat is a vanishing quantity at deviation 42° at the left of the scale (42° with a 60° prism at the temperature of $+20^\circ$ Cent., corresponding to a wave-length of $0\mu\cdot48$, or that of "blue" radiant energy). Confining our attention to the solid curve, we observe that it reaches a maximum near $39^\circ 40' = 1\mu\cdot5$, corresponding to rays of dark heat which are yet transmitted by glass, and which must be emitted from a source at a very high temperature. The maximum of the solar heat directly observed through the rock-salt train is found to be at the same point. There is no reason to doubt, then, that this maximum is due to the solar heat reflected from the lunar surface, and its actual effect is to produce a deviation of rather less than 20 degrees on the arbitrary scale of the galvanometer from the small part of the spectrum covered by the bolometer. Continuing to go down the spectrum in the direction of greater wave-lengths, and passing with casual notice a depression at $39^\circ 15' (\lambda = 3\mu\cdot1)$, which, it is probable, would be found in the direct lunar spectrum were there no intervening atmosphere, we come to a very large depression at $38^\circ 30' (\lambda = 7\mu)$, due almost beyond doubt to the rays emitted from the lunar soil having been here absorbed by our atmosphere. The conclusive evidence that this is due to the atmosphere is derived, first, from the constant appearance of an analogous band in the heat spectrum of the sky away from the moon, and, second, from the independent observation of the existence of this band in the invisible spectrum of a terrestrial object after absorption by 100 metres of air. In the latter case it is always found distinctly marked in moist weather and can even be observed under circumstances favourable to its development, in the few metres of air within the length of the observing-room. It is important here to remark that the maximum of the *unabsorbed* radiation of a Leslie cube, at a temperature a little below that of boiling water, is found at the deviation of $38^\circ 20' (\lambda = 8\mu)$, when observed by the same rock-salt train.

Following the solid curve down the spectrum, we find it rise into its principal maximum just below deviation $37^\circ 30'$

(λ , about 14^{μ}), where it attains a height of about 43 degrees of our arbitrary scale *. It is again most important to remark that this point, just below $37^{\circ} 30'$, corresponds to the maximum of the unabsorbed radiation of a lampblacked surface at a temperature of about -10° Cent. Were it not, then, for atmospheric absorption, we should assert with confidence that, so far as the radiations of a lampblacked surface and the lunar soil are comparable, the temperature did not exceed -10° Cent. Below this point the curve falls off with interruptions by several cold bands, until evidence of heat disappears near deviation 33° of our rock-salt train; but of this latter portion of the solid curve we will not pause here to speak. The dotted line is an attempted reconstruction of the original curve of lunar heat as it would appear before atmospheric absorption. It is made by allowing for the amount of absorption directly observed in the sky radiation, and in the radiation from terrestrial objects at a low temperature, already referred to, supplemented by an estimate of atmospheric absorption in this region inferred from a comparison of solar and electric arc radiation, to be presently described; and this constructive maximum occurs near deviation $38^{\circ} 15'$, which corresponds to the maximum of unabsorbed radiations from a terrestrial source at a temperature of a little over $+50^{\circ}$ Cent.

Direct observation, then, of the lunar heat-curve indicates that the probable temperature of the lunar soil is between 0° and -20° Cent. This is subject to the effect of our atmosphere, which probably is to displace this maximum in some degree towards the position of greater cold; but the highest temperature we can assign by an allowance for this is $+50^{\circ}$ Cent. Between these points, we believe it probable that the temperature of most of the lunar sunlit soil must lie. The temperature of the lunar poles has not been specifically determined, but direct observation indicates that it is still lower.

The relative amounts of the reflected solar and the emitted heat could evidently be obtained with satisfactory accuracy by measurements within the respective portions of the solid curve, were it not for the distorting action of the terrestrial atmosphere already mentioned. We must refer to the original

* It may be interesting to observe that we infer from our bolometric observations that the effect of the total and unconcentrated lunar radiation on a blackened thermometer would be something like $\frac{1}{1000000}^{\circ}$ Cent.

memoir for reasons for estimating the total amount of the reflected radiation as little more than $\frac{1}{7}$ of that emitted*.

The memoir, of which an abstract is here given, contains numerous subsidiary researches and observations for which we must refer the reader to the original, only here mentioning two:—

First. Temperature-correction of a rock-salt prism. This investigation of the change of refrangibility due to temperature was carried only far enough to give such approximate accuracy as served our immediate purpose, giving a value of $-13''$ of arc for each degree Centigrade; but subsequent measurements have materially modified this, and I give the value now adopted, which is $-9''.5$, the formula being

$$d_t = d_{20^\circ} - (t - 20) 10'',$$

where d = deviation, and t = temperature in Centigrade degrees.

Second. Comparison of the intrinsic intensity of solar radiation with that of the electric arc in different parts of the spectrum. This observation of the comparative intensity of the sun and the electric light is given in the original memoir only so far as to show that it brings independent evidence of a large atmospheric absorption of the extreme infra-red rays and enables us to estimate approximately the amount of this absorption at each point in the spectrum. The observations were not repeated to obtain such a thorough comparison as

* Lord Rosse found that 87 per cent. of all the solar rays were transmitted by a particular piece of glass which allowed 92 per cent. of solar light to pass, and 12 per cent. of the total lunar beam. He attempted from this to determine the relative amounts of the solar and lunar heat, but felt obliged, in the then state of knowledge, to make the assumption (which our subsequent researches have shown to be erroneous) that the glass absorbed *all* the invisible rays, or that the lunar radiation contains 12 per cent. of luminous rays, instead of less than 5 per cent., which is more nearly the actual case; but when Lord Rosse's own observations are reduced with the aid of the facts determined by the writers, and representing the actually large transmissibility by glass of the invisible rays of shorter wave-length in the infra-red, his expression for the relative value (which we will call x) of the emitted part of the lunar radiation (whose transmission by glass is presumed from observations on a Leslie

cube to be 1.6 per cent.) becomes $\frac{0.87 + 0.016x}{1+x} = \frac{1.2}{1.6}$, from which $x = 7.2$ times the reflected solar part; so that if Lord Rosse could have possessed, at the time his reductions were made, knowledge as to the diathermic properties of glass which has only been acquired since, his own observations would have given results for the relative amounts of reflected and radiated heat in somewhat remarkable accordance with our own.

would be desirable. As they have never been printed, however, and since, so far as we know, none other such exist, we will give them here under the caution that they are to be considered only first approximations. The light was that from the pit of the positive carbon of gas coke, one inch in diameter, with the current derived from a dynamo, actuated by an engine of ten horse-power, and therefore certainly at least as intrinsically hot and bright as any smaller arc-light in more common use, and presumably much more so. The apparatus was that already described in the memoir "On hitherto unrecognized Wave-lengths." *

The following Table gives the observed galvanometer deflexions after applying a multiplying factor for the shunt, which had to be used for the larger readings :—

1. Deviation Rock Salt 60° Prism.	2. Wave- length.	3. Observed deflexion <i>sun</i> after absorption.	4. Observed deflexion <i>arc</i> .	5 Calculated deflexion <i>sun</i> without absorption.	6. Observed ratio <i>sun</i> and <i>arc</i> .	Calculated ratio of unabsorbed <i>sun</i> and <i>arc</i> .
	μ	div.	div.	div.		
43 53	0.373	7.5	1.3	34	5.77	26.0
43 17	0.398	11.5	1.5	38	7.67	21.8
41 54	0.489	33.5	5.3	60	6.32	14.4
41 05	0.587	104.0	10.5	115	9.90	11.1
40 45	0.663	204.0	22.0	204	9.27	10.0
40 27	0.749	432.0	43.5	450	9.93	9.1
40 05	0.96	1 073.0	215.0	1 763	4.99	8.2
39 54	1.13	1 783.0	459.0	3 534	3.88	7.7
39 20	2.87	1 905.0	882.0	5 645	2.16	6.4
39 00	4.3	521.0	235.0	1 363	2.22	5.8
38 45	5.6	75.0	157.0	832	0.48	5.3
38 00	10.4	19.5	39.0	156	0.50	4.0

The result of the comparison of the (of course unabsorbed) electric arc with the radiation of the sun after absorption, as shown in the sixth column, is that this solar radiation in the orange and red is nearly ten times that of the arc, while towards the violet end of the spectrum the relative superiority of the absorbed solar heat diminishes, evidently because of the progressive increase of the atmospheric absorption in that direction, which lessens the solar intensity without sensibly affecting that of the arc. The solar efficiency continues greater through all the infra-red spectrum known until very lately, while in the extreme portions, recently investigated, it falls below that of the arc. This is partly due to the fact that radia-

* See this Journal, xxii. August 1886.

tion from a source at a lower temperature (the arc in this case) is relatively more powerful in the longer than in the shorter waves ; yet it can hardly be doubted that here also (that is, in the *extreme* infra-red) a very large atmospheric absorption has taken place.

There is reason to believe that a considerable part of this absorption takes place in the first few metres of air ; while we conclude from all the evidence in our possession, that the real telluric absorption, being a locally selective one, is much greater than the comparison of high and low altitude observations alone would indicate.

The import of this comparison will be still more evident from a consideration of the seventh column, where by means of the Allegheny tables of the solar absorption we have calculated the ratio of the arc heat to that of the sun before absorption by the earth's atmosphere. Although a large absorption by the solar atmosphere has already taken place, we see that in the ultra-violet the solar radiation is from 20 to 30 times that of the arc, while that of the absorbed sun is only about 6 or 7 times. When we reach the region of the red and upper infra-red, we see that these ratios are nearly the same in the absorbed and unabsorbed solar radiation, showing that the terrestrial absorption in this region (which was once supposed to be its principal seat), is in fact very small, while in the regions of the extreme infra-red corresponding to temperatures not greatly exceeding that of the terrestrial soil (regions only revealed by quite recent investigation) the telluric absorption again becomes considerable.

The general result of this comparison is to enhance our ideas as to the rate of solar radiation and as to the solar temperature. Comparisons of the total solar radiation with the total arc radiation have (it may be observed) been made before, but so far as I am aware, comparisons of the heat in different portions of their spectra are here presented for the first time.

Principal Conclusion.

Of the numerous conclusions to be drawn from this research, we here only direct the reader's attention to what we consider the most important one, namely :—That the mean temperature of the sunlit lunar soil is much lower than has been supposed, and is most probably not greatly above zero Centigrade.

Post Scriptum.

I would ask to be allowed here to state that the very considerable expense for the special means and reduction of the

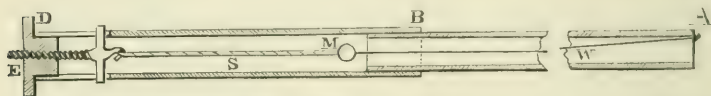
preceding series of lunar researches was born by one of the most generous and disinterested friends that Science has had in this country, the late William Thaw, of Pittsburgh. By his own wish, no mention of his name was made in previous publications in connexion with the results so greatly indebted to his aid. His recent death seems to remove the restriction imposed by such a rare disinterestedness.

IV. *On a New Electric Radiation Meter. (Preliminary Note.)*

By W. G. GREGORY, M.A., Demonstrator in Physics at the Royal Indian Engineering College, Coopers Hill.*

THE usual method of detecting electric radiations by observing the sparking across an air-gap in the wire used as a receiver admits of only a rough estimate of their intensity.

The object of this paper is to describe an instrument by means of which definite quantitative measurements may be made. It is based on the measurement of the elongation of a wire when heated by the currents induced in it by the rapidly varying field of force.



It consists of a long glass tube A B cemented to a shorter piece of brass tubing B D. Within is stretched a platinum wire W fastened to the glass tube at A and to a Perry magnifying-spring at M, where there is a mirror to indicate the rotation of the spring by the reflexion of a beam of light upon a scale. At E there is a nut and screw for adjusting the tension. The brass tube is partially filed away in front of the mirror to form a window. The object of the brass tube is to compensate the spring for general changes of temperature, the glass tube serving the same purpose for the platinum wire.

The wire employed was $\cdot 0086$ cm. in diameter, and 192 cms. long. The spring was about 25 cms. long and $\cdot 007$ cm. in diameter. It was made out of a fine kind of tinsel $\cdot 04$ cm. wide and $\cdot 0015$ cm. thick, which can be obtained at fancy shops wound loosely on cotton. When removed from the cotton, it was already in the form of an irregular helix. It was then rolled tightly between the fingers to reduce the diameter as much as possible. A piece of silk was next attached to one end, and the spring extended almost to breaking-point, the

* Communicated by the Physical Society: read November 1, 1889.

silk allowing it freely to untwist as much as it would. After this it was rolled between two hard surfaces and again pulled out. This was repeated till at last 10 revolutions per millimetre extension were obtained.

The mirror was a $\frac{2}{10}$ -inch worked concave one, and gave a very sharp image of a wire on a scale one metre off. Using an ordinary galvanometer-scale, it was easy to read to one division. This would correspond to an elongation of the wire of $\cdot 000005$ of a millimetre, and a rise of temperature about $\cdot 003$ of a degree Centigrade. In spite of this sensitiveness, only one or two divisions' deflexion were obtained with the oscillator 4 metres off. The oscillator used consisted of two brass rods $\cdot 53$ cm. in diameter supported horizontally and carrying two zinc plates 40 cm. square, capable of sliding along them so that the wave-length could be altered at pleasure. They were usually kept about 25 cm. apart. The terminal knobs were 2 cm. in diameter and the spark-gap about 2 or 3 millim. It was noticed that one of the knobs blackened very quickly but remained quite cool, while the other, which altered little, became very hot.

The induction-coil employed to work it was 20 cm. long and 12 cm. diameter, and gave with the battery-power employed sparks 4 cm. long between two points. To obtain greater regularity in the working of the coil, a tuning-fork mercury break, vibrating 86 times a second, was used.

By employing a larger coil larger deflexions could, no doubt, be obtained and effects at greater distances observed.

A method was tried for increasing the sensitiveness by weighting the mirror so that its centre of gravity was behind and rather above the axis of suspension. The tension was adjusted so that the spring kept the mirror near its position of unstable equilibrium. The effect was to render the smaller deflexions nearly 10 times as great, while the sensitiveness diminished as the deflexions became larger. But the difficulties of working with it were greatly increased, as the smallest draught of air would alter the zero-point.

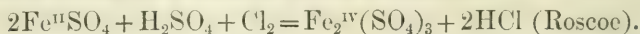
Wires of different materials were also tried which should theoretically give better results; but, probably owing to their diameters not being sufficiently fine for the tension to which they were subjected, the results were not satisfactory. The convenience of being able to compensate the platinum wire by the glass tube seems, however, a great point in favour of the use of platinum, and has led me hitherto to keep to it.

V. *On Electrifications due to the Contact of Gases with Liquids.* By J. ENRIGHT, B.Sc.*

A STUDY of Helmholtz's theory of atomic charges led to the experiments I am about to describe. When one has got the idea that molecules are kept in their integrity by the mutual attractions of the oppositely charged atoms or radicals composing them, a question soon arises as to what part, if any, these charges play in ordinary chemical reactions. The theory precludes any other form of chemical affinity than that due to the mutual attractions of the opposite charges, and it occurred to me that since at the moment of reaction there must be disturbance and re-arrangement of them, some indication of their existence might be obtained by allowing reactions to go on in an insulated vessel properly connected with a quadrant-electrometer. Even if a permanent electrification could not follow, I thought it just possible that a momentary flutter of the "spot" might take place on account of the electric disturbance due to the interchange of the charged ions.

This consideration alone was sufficient to excite one to experiment, but if I tell the whole story I must say that I had had other expectations. According to theory the charges on monads are exactly equal. How then does it happen, if reactions be a result of the charges, that chlorine drives iodine out of potassic iodide? How, indeed, does it happen that any one molecule composed of a particular pair of monad elements is stronger,—that is to say, more stable than any other molecule composed of any other pair of monads? And so on. After pondering on such questions for some time, I could not suppress the thought that after all perhaps the charges might not be equal, and that the experiments I had determined to carry out might possibly throw some light on the matter.

Then there were certain special reactions which appeared to afford an admirable opportunity for experimental study of the theory. I refer to cases in which the atomicity of elements undergoes a change during a reaction,



Here four monad charges of positive electricity attached to the iron on the left change into eight monad charges on the same quantity of iron on the right. If the increment of positive electricity be produced by contact an equal charge of

* Communicated by the Physical Society : read November 15, 1889.

negative ought to be set free, and this ought to be easily detected by the electrometer.

On the whole there appeared, to a strong believer in the theory, a fair and inviting field for experiment. My plan was to examine in the manner indicated instances of the four following types of chemical change :—

- (1) Combination of elements.
- (2) Displacement.
- (3) Double decomposition.
- (4) Change of valency.

I may as well say at once that from (3) and (4) I got no result whatever, from (1) only an electrification of little importance, and that it was from (2)—instances of displacement—that the results I wish to call attention to were obtained.

The electrometer was made rather sensitive. A high-resistance Daniell through which a current never passed gave a deflexion of 94 divisions either way. An insulated plate on which the reactions were to proceed was fixed so that it could be connected or disconnected at pleasure with the insulated pair of quadrants. The insulation of this plate was tested by giving to it a small charge, and connecting it then with the quadrants. The spot moved and came to rest 200 divisions from zero. It was watched for 3 minutes, during which it maintained its position.

A porcelain dish containing about 20 c.c. of a strong solution of potassic iodide was placed on the insulated plate. About the same volume of a strong solution of chlorine in water was placed in a beaker to which was attached a handle of insulating material, and by means of this handle the chlorine water was poured into the potassic iodide. A heavy brown precipitate appeared. The insulated plate was now connected to the insulated quadrants. No deflexion resulted. The experiment was repeated without producing a movement of the spot.

The porcelain dish was now half filled with distilled water, placed on the insulated stand, and a fragment of potassium cast into it. The usual reaction ensued and the "spot" moved 160 divisions to the left, came to rest, and maintained its position. The quadrants were short-circuited, and the spot returned to within 2 divisions of zero.

At first view this appeared exactly what I had expected to occur. On reflection, however, many possibilities suggested themselves and each had to be considered. Had I merely detected electricity in the air? May not the deflexion be due to the inductive action of the charged needle on the

quadrants? Was the escaping hydrogen electrified, and if so what was the sign of the charge? I proceeded to repeat the experiment.

The quadrants were short-circuited, and the insulated dish, after being momentarily put to earth, was, as before, connected to the insulated quadrants. A second fragment of potassium was tossed into the water in the dish. The spot moved 28 divisions to the left, then turned and moved up the scale to the right, coming to rest at 200 divisions from zero. The quadrants were once more short-circuited, and the experiment again repeated. The spot moved 40 divisions to the right. I could not possibly explain such irregular behaviour. I carefully looked up the connexions and tested the instrument. It was in good order. I again repeated, but with similar results.

Sodium was used instead of potassium, and although the deflexions with it were also irregular, the tabulated results showed a contrast. When sodium was used, 40 per cent. of the deflexions were first to the left; when potassium was used, 70 per cent. were first to the left. Speaking broadly, this seemed to indicate that when potassium was used the dish received a negative charge, when sodium was used the dish took a positive charge; and as I fancied that such a result would enable me to set up some theory with regard to the atomic charges, I tried very hard to eliminate what I then believed to be accidental exceptions and to prove that in reality such was the case.

The porcelain dish was replaced (1) by a glass beaker, and (2) by a metallic dish, the experiment being repeated in every other particular, but without obtaining greater regularity in the deflexions.

I wish to remark here that the method of testing the electrification by keeping the insulated vessel from which gas is escaping in connexion with the insulated quadrants during the reaction is faulty, inasmuch as that under the circumstances a deflexion may be caused by the inductive action of the charged needle on the quadrants. It has, however, this great advantage, viz., that one can see distinctly every variation that may take place during any interval. It will be noticed that throughout the inquiry I use this method for preliminary testing, and that I conclude nothing until I verify by the more rigid process of allowing the reaction to go on while the insulated plate is disconnected from the quadrants, and testing the electrification at its close.

Having failed to get a definite and constant result with water, I proceeded to try other liquids. Sodium and dilute

sulphuric acid, sodium and nitric acid, and many other such combinations were tried, and eventually I found that sodium and strong acetic acid gave an *invariable* result, viz., a positive charge on the dish in which the reaction took place. This has not failed hitherto in a single instance.

I reviewed the state of affairs. The first thing to do, as it appeared to me, was to ascertain whether or not the hydrogen carried a charge, and, if so, to determine its sign. I found it so difficult to work with sodium that after many unsatisfactory attempts I decided to search for another metal which would give a similar constant and definite result. One naturally turned to zinc.

A piece of zinc was thrown into dilute sulphuric acid which was put into the insulated dish, the connexions being as already described. The spot rapidly moved 36 divisions to the left, turned, went back across zero and up on the other side 120 divisions. This was not encouraging. It seemed to be the beginning of another set of irregular deflexions. It, however, went to show that electrification was an accompaniment of most chemical reactions. I repeated the experiment several times, varying the degree of dilution of the acid, but failed *then* to get constant results. I next tried hydrochloric acid.

A small portion was placed in the insulated dish and a particle of zinc thrown into it. The spot rapidly moved off the scale to the left, indicating a negative charge on the dish. The quadrants were short-circuited, and the spot returned to zero. Repetition was followed by the same result, and fortunately this turned out to be as constant a deflexion to the left as that from sodium and acetic acid was to the right, while it was much greater in quantity.

I now concentrated my attention on zinc and hydrochloric acid. In this experiment, as in all others where a gas escaped into the air, it was possible, though not likely, that the resulting deflexions were due to atmospheric electricity, and I thought it as well to settle this point at once. A piece of sponge was saturated with alcohol and placed on the insulated plates. It was then fired, and burned with a large flame. The insulated plate was connected to the quadrants when the sponge ceased to burn, and the spot at once moved 10 divisions to the right, indicating a small positive charge on the plate. The experiment was repeated in every particular except the burning of the sponge, but with the result of only a disturbance of the spot of a few divisions.

The air in the neighbourhood of the insulated plate appeared to be slightly electrified, but as it was of opposite

sign to the charge produced by the action of zinc and hydrochloric acid, it was certain that the latter was not due to any atmospheric cause. But a new point of great importance had arisen. Whence came the positive charge in the air near the instrument? The idea of its being due to the evolved hydrogen at once suggested itself. For some time before testing with the sponge, I had been repeating the experiment with zinc and hydrochloric acid in order to satisfy myself as to its constancy, and a considerable quantity of hydrogen had escaped into the air.

The charge on the evolved hydrogen opposite in sign to that on the insulated generator! If this were really the case I saw that I should have to give up certain ideas which I had been fostering while dealing with these experiments. The point had to be at once cleared up.

A zinc goblet was metallically attached, mouth downwards, to the insulated plate. A long-necked flask containing zinc and hydrochloric acid was placed underneath in such position that the hydrogen found its way into the inverted goblet. In two minutes after so placing the hydrogen generator the goblet was tested by connecting it with the insulated quadrants. The spot moved 78 divisions to the right, indicating that the hydrogen escaped with a positive charge—that is to say, as already suspected, its charge was opposite in sign to the acid and generator from which it was evolved.

The experiment was several times repeated, and always with the same result, but it was noticeable that the positive charge on the hydrogen was much less in quantity than the negative charge on the generator. If they were in reality oppositely charged, the quantities, as in all such cases, would be exactly equal. I urged, in explanation, that the hydrogen moving over the moist glass of the long-necked generator must lose some of its charge. However, a confirmatory experiment was devised.

A second insulated plate was set up and connected metallically with the first. A hydrogen generator, containing zinc and hydrochloric acid, was placed on one, and a suitable pneumatic trough was placed on the other, in such manner that the gas might be generated and collected on the insulated plates, which were connected to the insulated quadrants. A stream of hydrogen was allowed to pass, and by means of an insulating rod the delivery-tube could be placed so that the hydrogen might get into the air or be collected and retained on the insulated plates at pleasure. It was found that as long as the gas did not escape the spot remained motionless, but that when it escaped from the plates into the air the spot

moved. This, I took it, proved that the charges on the generator and evolved gas were equal in quantity, though opposite in sign.

The state of the case was now, so far, pretty clear. When hydrogen was produced by zinc and hydrochloric acid the hydrogen became positively, the generator negatively, charged. I set this fact up before my mind and examined it as carefully as I could on every side. I turned it round and round, looking for some information as to the atomic charges, but I could find none. Had the charge on the escaping gas been of the same sign as that on the generator, I could have set up some hypothesis concerning them, but, as things were, nothing of the kind was possible.

But what is the cause of this undoubted electrification? I repeated the experiment many times. I varied the quantities of acid and zinc, and noticed that with weaker acid or a larger quantity of zinc the deflexions were not so strong. During these repetitions I was in the habit of short-circuiting the quadrants when the spot came to the end of the scale, lest the suspending fibres of the needle should get a *set* from being twisted too much in one direction. On one occasion, however, being called away suddenly, I neglected to do so, and the electrification worked its will, so to speak, on the needle. On returning in about twenty minutes, I found that all the zinc was dissolved, and to my very great astonishment the spot was at rest at the extreme right of the scale.

Up to that time the deflexion from zinc and hydrochloric acid had been to the left; and, as I had made the experiment a great many times with this unvarying result, I was much perplexed. The uncertain behaviour of sodium and potassium was still fresh in my memory.

However, what to do on the occasion was quite clear: I repeated the experiment in every particular, sat down, and watched it. The spot went rapidly off the scale to the left as usual. The reaction proceeded. In eleven minutes the spot appeared again on the scale, went down 100 divisions rather slowly, then more rapidly, crossed the zero, and at a good pace went up the other side almost to the end of the scale. This was quite a new development. Frequent repetition, with the same result, proved that this behaviour, strange as it was, had a definite cause. I varied the strength of the acid and the quantity of zinc, and found that by either making the acid weak or increasing the quantity of zinc I could hasten the reversal of the sign of the electrification of the generator.

I now concentrated my attention on this reversal of sign. I contrasted all the circumstances attending the deflexion to the left with all those attending the deflexion to the right, and could detect only one difference, and that was the production of chloride of zinc in the generator, and I could not fail to see that as the quantity of this salt increased the deflexions to the right became stronger.

From this change of sign of the generator, when a certain quantity of chloride of zinc got into solution, there suddenly appeared to come a ray of light which I thought dispelled the fog which hung round the earlier experiments. The nature of the liquid through which the hydrogen passed apparently determined the sign of the electrification. I paused again to review the events of my little enterprise.

I set out in quest of some direct evidence as to the atomic charges. I had tried the four types of chemical change. From double decomposition and from cases of change of valency I had got no result whatever. From direct union of elements—from the combination of phosphorus and iodine, accompanied by a cloud of P_2O_5 , and, I suppose, iodine vapour—I had got an electrification. From many cases of displacement I had got considerable electrifications; but from some, such as the displacement of iodine by chlorine, I had got nothing whatever. A careful examination of these results disclosed the fact that no electrification was obtained except when something escaped from the vessel in which the reaction occurred. This circumstance I thought could not fail to have some meaning. Then there were the leading incidents, as I considered, of the inquiry:—(1) The escaping gases or vapours came off with a charge opposite in sign but equal in quantity to that on the generator. (2) The reversal of the sign of both generator and escaping gas when the liquid in the generator underwent a definite change.

Such were the facts to be brought under some theory. I was reluctantly compelled to conclude that they had nothing to do with atomic charges, but for all that they afforded food for the most delightful contemplations, often for hours at a stretch, during the last two or three years.

Reflect as I may on the reversal of sign of the electrification when a certain quantity of chloride of zinc gets into solution, I can find no explanation for it but the electricity of contact. Hydrogen is positive to hydrochloric acid, but negative to chloride of zinc. And, indeed, looking at the whole matter in this light, from my present standpoint, I can perceive how, in the earlier experiments, the nature of the liquid

through which the hydrogen passed decided the sign of the electrification. From hydrochloric acid it was positive; from acetic acid (or it may be acetate of sodium) it was negative. Even the very whimsical deflexions from sodium and water become intelligible. As a piece of sodium careers about on the surface of water, the escaping hydrogen is one instant in contact with water, the next with caustic soda, the next with the side of the vessel, and, accordingly, on the theory of contact, the irregular deflexions are at once explained.

In most of the experiments described above, the hydrogen was allowed to escape from an open dish or beaker, and not from a narrow delivery-tube, for it was found that the gas partially discharged itself when it passed through narrow openings. Whatever tended to electrically connect the charged liquid with the oppositely charged escaping gas, also tended to lessen the charges on both. And besides this, there was the possibility that the contact of the gas with the delivery-tube might cause electrification. On the whole, it was found least ambiguous to half fill an evaporating-dish about 6 inches in diameter and 2 inches high with HCl and drop into it a few fragments of zinc. The bubbles of gas then shot straight up through the middle of the liquid, and passed into the air without coming into contact with anything else. It was, however, a defect of this mode of proceeding that particles of the acid were projected about in all directions, sometimes beyond the dish. In order to get rid of any doubts on this head, a smaller dish was used and placed at the bottom of a beaker 7 inches high. I propose to give in detail one of several experiments made in this way with all possible care.

The electrometer was *not* in a very sensitive state. The high-resistance Daniell gave a deflexion of 38 divisions on either side. A glass beaker 7 inches high and 5 inches in diameter was placed on the insulated plate. A porcelain dish, $2\frac{3}{4}$ inches in diameter and $1\frac{1}{8}$ inch high, was nearly filled with a 10-per-cent. solution of HCl in distilled water, and placed at the bottom of the beaker just mentioned. Three small fragments of zinc were now dropped into the dilute acid in the small dish. A very slight effervescence at once appeared, and it gradually increased, but never became violent. No trace of spray could be detected at the end of the experiment above the lower half of the beaker. In 4 minutes from dropping the zinc, the spot could be perceived moving, and in $4\frac{1}{2}$ minutes more it had moved 28 divisions to the left, indicating the charge on the dish negative. I append the notes taken during the time the experiment lasted.

	Time.		Reading.
	h	m	
Zinc dropped into acid. Insulated quads connected to insulated generator	2	10	378 (zero)
Spot moving to left. Generator positive	2	14	377
Spot moving faster	2	16	367
	2	17	360
Insulated quads and insulated generator disconnected	2	18½	349
	2	19½	349
Insulated quads and generator reconnected	2	20	329
	2	21	322
Spot stops and appears to return	2	21½	319
	2	23	328
	2	25	346
	2	26	366
Spot crossed zero	2	26½	378
	2	28	388
Quads and generator disconnected	2	31½	458
	2	33	458
Quads and generator reconnected	2	33½	513
Effervescence gets less	2	35	550
	2	37	562
	2	40	568
Quads short-circuited	2	42	382 (zero)

It may yet be urged that when hydrogen passes through hydrochloric acid, it carries with it both HCl gas and vapour of water, and that the electrification is due to these, and not to the hydrogen. In order to test the suggestion, I placed on the insulated plate a dish nearly filled with boiling concentrated HCl. In two minutes the plate was connected with the insulated quads, but the spot moved only 1 or 2 divisions. It was then watched for more than 5 minutes, but the spot did not stir although clouds of vapour were escaping from the acid.

I cannot help remarking on the difficulty of neutralizing a gas—at all events, hydrogen. The following experiment is well calculated to illustrate this properly, while it affords, I submit, a very stringent verification of the experiment to which the notes are appended. The large beaker with the small dish was set up in the manner described in the experiment just referred to. The dish was nearly filled with a 16-per-cent. solution of HCl in distilled water. Three small fragments of zinc were thrown into it. A disk of sheet zinc with a circle one inch in diameter, cut from its centre, was placed as a cover on the beaker. Over the aperture in the centre were placed, one above the other, 4 flat pieces of perforated zinc, the perforations being $\frac{1}{16}$ of an inch in diameter. The hydrogen had to fight its way through this barrier, and

yet it carried with it the greater part of its charge, as the following notes of the experiment prove. The high-resistance Daniell gave a deflexion of 72 divisions either way.

	Time.		Reading.
	h	m	
Zinc dropped into acid. Cover placed on beaker.	3	23	365
4 flat zines placed over aperture		25	364
		27	363
		28	358
		29	343
Spot comes to rest and returns		30	333
		31	333
		32	343
		33	353
		34	363
		35	373
		36	383
		37	383
		39	413
Effervescence ceasing	3	42	413
Quadrants short-circuited	3	43	368

On examining the perforated zines used in this experiment, each was found to have either spray or condensed vapour deposited on it, but the quantity on the lowest one was greater than that on any of the others. I was not, therefore, clear as to what part the spray played in the matter, and I set myself to consider what experiments I could make to clear up the point. Eventually I decided to make the following two, which I submit as decisive:—

(a) Every one has noticed that when hydrogen escapes from a generator containing acid and zinc, particles of the former are projected with considerable force from the vessel. I easily succeeded in catching these particles, or some part of them, on the metallic part of a proof-plane. I then touched the electrode of the insulated quads with the proof-plane, and found that the charge produced a deflexion to the left, indicating that the spray was of the same sign as the generator, and consequently opposite in sign to the charge carried by the gas. It also appears from this experiment that electrical repulsion among the particles themselves constitutes part of the force which causes their flight through the air.

(b) The bottom of a metallic goblet was perforated with holes about $\frac{1}{8}$ inch in diameter. It was then attached, mouth downwards, to the electrode of the insulated quadrants. A hydrogen-generator containing zinc and HCl was placed under it in such a position that the evolved gas passed right through

the goblet. Almost instantly the spot moved rapidly to the right, which I had expected. The generator was now withdrawn. The spot slowly returned to within 5 divisions of zero.

Now if the electrification were due to spray, the goblet would retain its charge (the insulation was good); but being due to the hydrogen, which gradually passed through the perforations into the air, it very rapidly lost it.

In the course of these experiments I had often cast about for means of measuring the difference of potential arising from the contact of zinc and hydrochloric acid, and on consideration it appeared to me that this experiment presented a possible method. Particles of matter charged with electricity, and impinging on an insulated conductor, to which they give up part or the whole of their charges, could not raise the conductor to a higher potential than they had attained; but they, in the course of time, ought to bring it up to that level. My notion was to allow the charged hydrogen to flow through the goblet, fixed as described, long enough to ensure its reaching the potential of the gas; then to remove the generator, and allow the gas to pass away through the perforations. The permanent deflexion then obtained ought, I considered, to be the measure of the quantity in question. I carried out with all the care possible several experiments on these lines; but on account of the tenacity with which the gas holds its charge, I failed to get satisfactory determinations.

At this stage of my inquiry, I felt that I had got a few definite facts, that I had cleared up, at all events to my own satisfaction, many points which were at first doubtful, and that the theory of contact which I proposed was consistent with all the observations I had made. I proceeded to devise new experiments with the view of testing the truth, and determining the scope, of this theory.

Hydrogen passing through HCl and H_2SO_4 takes a positive charge; passing through the corresponding salts of zinc it takes a negative charge. Then at any moment it ought to be possible to reverse the electrification by introducing into the vessel in which the reaction is going on acid or salt, as the case may be. The old experiment was made. Hydrogen was escaping from a 16-per-cent. solution of HCl , and the spot had travelled 100 divisions when a strong solution of zinc chloride was added. The spot went quickly back and up on the other side of the scale, showing that reversal had taken place. The addition of HCl produced a second reversal.

I had found hydrogen positive to two acids, and a question as to whether this was general often floated before me. I had

no means of testing with nitric acid, because its action on metals does not give rise to hydrogen—at all events not in the final stage. I therefore directed attention to the other side of the question. Hydrogen was proved to be negative to chloride and sulphate of zinc. Was it possible that it was negative to other salts, or to salts in general?

I again made the old experiment with $\text{Zn} + \text{HCl}$, and when a deflexion of 50 divisions was obtained a strong solution of ferric chloride was added, with the effect of reversing the sign of the electrification. I proceeded to try other salts, such as NaCl , AmCl , FeSO_4 , MgSO_4 , CaCl_2 , and found that these also produced reversal. I found, however, a few salts which did not do so, notably $\text{Co}(\text{NO}_3)_2$.

A wide principle thus appeared to be foreshadowed, viz., that hydrogen is positive to acids but negative to salts; but the number of cases examined does not warrant one in laying it down absolutely. Moreover, I have found the hydrogen passing from acetic acid, whether by the use of sodium or iron filings, always comes off with a negative charge. I strongly suspect, however, that the reversal of sign in these cases takes place so rapidly that it escapes observation. I have had several instances of the spot moving a small distance to the left, suddenly turning, and moving far up on the opposite side of the scale. Occurrences of this kind leave no doubt on my mind that the first electrification (that due to the gas passing through the acid) is often small, owing, I think, to the rapidity with which the salt produced in the reaction diffuses.

Is hydrogen among gases unique in becoming charged when it passes through acids? was the question that next presented itself. I considered what reactions were likely to give any information with regard to the matter, and made numbers of experiments in the manner already fully described. I found that as a rule electrification results from any reaction giving rise to an escape of any substance into the air. In many cases the electrification is very trifling, and the electrometer must be in a sensitive state in order to show it. Of all the reacting combinations which I have tried, $\text{HCl} + \text{Zn}$ give by far the greatest difference of potential between generator and expelled gas. On the other hand, from $\text{H}_2\text{SO}_4 + \text{NaCl}$ I failed to get any trace of electrification. I give in the following Table *only* those reactions which by frequent repetition I have found to give constant results. I also give the estimated difference of potential, but shall postpone to a later stage a description of the method of making the measurement.

Reacting substances.	Escaping gas.	Gas passing		Quantity D. P. in volts.
		Through acid.	Through salt solution.	
1. $\text{HCl} + \text{Zn}$	H	+	—	42
2. $\text{HCl} + \text{CaCO}_3$	CO_2	+	—	
3. $\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3$	CO_2	+	—	9
4. $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_3$	SO_2	+	—	
5. $\text{HCl} + \text{Na}_2\text{SO}_3$	SO_2	+	—	
6. $\text{H}_2\text{SO}_4 + \text{Zn}$ (50% acid)	H	+	—	16
7. $\text{HCl} + \text{FeS}$	SH_2	+	—	
8. $\text{H}_2\text{SO}_4 + \text{FeS}$	SH_2	+	—	
9. $\text{HCl} + \text{Bleaching-powder}$	Cl	+	—	
10. $\text{H}_2\text{SO}_4 + \text{Bleach.-powder}$	Cl	+	{ Could not get this to reverse.	
11. $\text{HNO}_3 + \text{Bleach.-powder}$	Cl	{ Could not get the usual positive deflexion.		
12. $\text{HNO}_3 + \text{CaCO}_3$	CO_2	{ Could not get positive deflexion.		
13. { CH_3 $\text{COHO} + \text{Na}$	H	{ Could not in either case get the normal positive deflexion.	—	
14. { CH_3 $\text{COHO} + \text{Fe}$	H		—	
15. $\text{H}_2\text{SO}_4 + \text{CaCO}_3$	CO_2	+	{ Could not get the reversal.	
16. $\text{H}_2\text{SO}_4 + \text{NaCl}$	HCl	Nil		

It will be seen that there are nine instances in which the electrifications occur normally—that is to say, in which the charge is of one sign when the ejected gas passes through acid, but of the opposite sign when the corresponding salt gets into solution. I wish to direct special attention to the instances of abnormal behaviour, which I believe to be entirely due to the solubility of the salts produced in the reaction. When these get rapidly into solution and diffuse through the acid, the electrification due to the gas passing through acid cannot be obtained. There are two cases with HNO_3 and two with acetic acid where this happens, and we know that the salts derived from these acids are very soluble. On the other hand, there are two cases where H_2SO_4 takes part in the reaction, in neither of which could the electrification due to the passage of the gas through the solution of salt be obtained. In both instances sulphate of calcium is formed, and we know that this is rather insoluble. The ejected gas therefore never passed through a solution of salt. My contention here derives great support from the fact that when Na_2CO_3 is used with H_2SO_4 to give CO_2 , both deflexions are obtained. The

only difference between the two reactions is that Na_2SO_4 is very soluble compared with CaSO_4 .

Taking a broad view of these experiments, they appeared to me to indicate that, in general, gases were positive to acids, but negative to solutions of salts. I could not, however, throw off a feeling of dissatisfaction which arose from my not being able to suggest a trace of any *à priori* reason for such a thing. I fancied I saw some reason why hydrogen should be positive to acids and negative to salts; but that the generalization should be so wide as to extend to all gases, seemed to me most improbable. I felt disposed to question my theory of contact altogether, and resolved to make experiments of a different kind for the purpose of testing it.

If hydrogen be positive to hydrochloric acid, then, why not, I asked, prove it by a straightforward experiment such as passing a stream of the gas through the strong acid? Two insulated plates were set up near the electrometer and connected by a piece of copper wire. A beaker 2 inches in diameter and 5 inches high containing strong HCl was placed on one, and a hydrogen generator furnished with a narrow delivery-tube more than 12 inches long was set on the other. The delivery-tube was suitably fixed, and a brisk current of hydrogen passed through the strong hydrochloric acid. The hydrogen was found to come off with a positive charge, but on allowing it to get into the air direct from the delivery-tube it also came off charged in the same way. Here, then, I was balked. Of course the object of the long delivery-tube was to neutralize the gas before it touched the strong acid in the beaker. I have often remarked how firmly the hydrogen held its charge, but I was quite unprepared to find that it passed through more than 12 inches of wet glass tubing $\frac{1}{8}$ of an inch in diameter and escaped strongly electrified. I next passed the hydrogen through a wash-bottle, but it again came off charged. I passed it through all manner of bent tubing, made all possible shifts in fact to de-electrify the gas in order to fairly carry out my experiment, but without success. In sheer desperation I snatched up a litre-flask, filled it with water, and displaced the latter at the pneumatic trough by hydrogen from $\text{Zn} + \text{HCl}$. I then placed the flask mouth upwards and open on the insulated plate which was connected to the quadrants. The spot gradually moved to the left, and came to rest at a distance of 180 divisions from zero.

This experiment yielded more food for thought. At first sight the deflexion appeared to be in the wrong direction, and I had to consider whether the hydrogen could, by any possible process, be neutralized.

I refilled the flask with hydrogen from zinc and hydrochloric acid and corked it before lifting its mouth from under the water, set it on the table, left it for $1\frac{3}{4}$ hours, then uncorked it and placed it on the insulated plate. A deflexion to the left of 100 divisions was gradually produced as the hydrogen left the flask. By repeated trials I found that it required from four to six hours to neutralize a flask or even a metallic vessel filled with hydrogen from zinc and hydrochloric acid.

But what of the deflexion in the wrong direction? On reflection, the explanation of the deflexion being to the left—that is to say, the insulated quadrants being negatively charged—very quickly appeared. The flask was held in the hand while being filled with hydrogen holding a positive charge. This acted inductively, repelling an equal quantity of positive to earth through my hand and body, and binding on the outside of the moist flask a charge of negative. When the flask was set on the insulated plate the hydrogen, owing to its lightness, gradually escaped into the air carrying its charge with it; and for every portion of the positively charged gas which left the flask a corresponding part of the negative charge bound on its wet outside was set free and spread over the quadrants, causing the deflexion. In fact the wet flask containing the charged hydrogen constituted a veritable Leyden jar.

I was anxious to verify this view. A hydrogen generator with a long neck and containing $\text{Zn} + \text{HCl}$ was placed on the table. A large wide-mouthed wet flask was attached to an insulating handle, and, by means of this handle, was held mouth downwards in such position that the hydrogen from the long-necked generator filled it by displacing the air. It was then taken by means of the insulating handle *near* the insulated plate (which was connected to the insulated quadrants), when the spot moved along the scale to the right, indicating that the quadrants were positively charged by the inductive action of the charged gas. The flask was next touched on the outside by the finger and again held *near* the insulated plate, but the spot did not move. This was quite in accordance with the Leyden-jar view, for the bound charge on the outside of the flask could have no effect on the insulated plate or the quadrants connected with it. The flask was now placed on the insulated plate, mouth upwards, and as the hydrogen escaped into the air the spot moved up the scale to the left, indicating that the bound negative charge on the outside of the flask was being liberated and charging the quadrants.

This afforded an instance of a kind of distribution of static electricity rather novel. I could only liken it to ground sul-

phur electrified by the grinding. Most instances of charged bodies are connected with surfaces, but here appeared a case where electricity pervaded an enclosed space. The only way in which I could figure it in my mind in connexion with the hydrogen was by furnishing each molecule of the gas with a charge with which it could not part until, in the ordinary movements of the molecules (according to the dynamical theory of gases) each came into actual contact with the moist inner surface of the flask containing the gas. This way of looking at it enables one to understand the slowness with which the electrified hydrogen becomes neutral; and as the time required to neutralize a vessel of gas of given shape and dimensions must be a function of the average velocity of its molecules at the existing pressure, suitable experiments may, possibly, lead to a direct determination of this quantity.

Musing over these experiments, the wet flask holding the charged hydrogen appeared, to me, not to differ materially from a soap-bubble blown with hydrogen from $Zn + HCl$. If there be anything in the notion, such a bubble should constitute a charged condenser with the binding charge completely enclosed. During the process of blowing it the repelled charge would pass to earth through the wet delivery-tube and generator. Figuring such a condenser floating through the air, I speculated as to how it would behave itself. As long as it remained in its integrity, no manifestation of its electrical condition could be given. Should the film, however, get fractured its nature would display itself. The gas containing the binding charge would instantly pass away, leaving the bound charge free on the water composing the shell, and it would pass to earth at the first opportunity.

Accounts have been given from time to time of curious bodies which make their way into dwelling-houses during periods of electrical disturbance in the air. They are described as gliding about, apparently examining nooks and corners, and often going up the chimney exploding (as it is called) on the way. Now if we consider a portion of electrified air enclosed by a film of some substance such as water, it would in most respects behave like a soap-bubble blown with hydrogen from zinc and hydrochloric acid. Being of nearly the same density as air, it would not rapidly ascend but move about, impelled by every slight draught. It would be a charged condenser, and the moment any rough or sharp prominence fractured the film, the bound charge would pass to earth, doing mischief in its track. Such an enclosure of electrified air might possibly be effected by an abnormal distribution of heat similar to that indicated by the formation

of hail during thunderstorms. So close did the resemblance between my soap-bubbles and those "fire balls," as they are sometimes called, appear to me that I hastened to ascertain by experiment whether or not my speculations with regard to them comprised any truth.

Soap-bubbles were accordingly blown by means of the generator containing $\text{Zn} + \text{HCl}$. Only small ones could be obtained, and these shot away towards the ceiling so quickly that it was not easy to touch them with the metallic part of the proof plane. Some few, however, were caught and the proof plane was found to be very slightly negatively electrified. Some better plan had to be tried. The end of the delivery-tube was placed under the surface of the soap solution while gas was escaping. A great mass of bubbles were produced on the surface, and some of them toppled over the side of the dish and fell towards the floor on account of the greater quantity of water in them. These were caught on the metallic part of the proof plane, and on testing the latter it was found to be strongly charged, the sign being negative, which bore out the idea of the bubble being a charged condenser.

Another form of the experiment then occurred to me. The dish containing the soap solution was attached to an insulating handle and then set on the table. The end of the delivery-tube was once more dipped into the soap mixture, and a mass of bubbles was as before produced. The delivery-tube was then withdrawn, and the dish lifted from the table by an insulating handle. It was kept thus insulated until, in the course of a few minutes, the bubbles broke up, allowing the hydrogen to escape. The dish was then tested and found to have a negative charge. The soap-bubble blown as described was thus proved to be a charged condenser.

If by any process a mass of electrified air were enclosed by vesicles of water, or any other conducting material, a free charge would be developed on the outside which would cause the whole mass to be attracted or repelled according to the electrical state of proximate objects. In a recent number of 'Nature' I find an account of a thundercloud behaving in a manner at once explained by this hypothesis. The observer describes it as appearing to detach itself from a mass of cloud, gradually descend, and immediately after draw itself up again. The descent would be due partly to the attraction of the earth and to the repulsion of similarly electrified clouds above it. On touching the earth the free charge would escape, and the clouds, which at first repelled, would now attract, it, causing its ascent.

If such an enclosure of electrified air as I suggest were to occur at a high temperature in the upper regions of the atmosphere, its potential would gradually rise as it cooled and descended towards the earth; for the cooling of the mass of air, and the increase of pressure due to its less elevated position, would cooperate to lessen its volume, and, therefore, the surface of the enclosing film, while the quantity of electricity would remain the same.

Up to this stage I had used glass vessels in these experiments, but according to the view just set forth there could be no reason why a metallic vessel should not behave in precisely the same way. A tea-canister was accordingly filled with hydrogen by displacement of water from a generator containing zinc and hydrochloric acid. It was then placed on the insulated plate, mouth upwards, and it was found that as the hydrogen escaped into the air the spot moved to the left, as had been expected; and it was found on trial that everything that had been done with the glass flask could be done with one of metal. We have thus a condenser with only one conductor, and apparently without a dielectric; and, from the ease with which it can be charged, and most of the properties of condensers demonstrated by means of it, one which may turn out useful for teaching-purposes.

A metallic flask filled with hydrogen by displacement of water from a generator containing $\text{Zn} + \text{HCl}$ I found very instructive. It proved that hydrogen holds its charge with unexampled tenacity, for the vessel could be handled or left in communication with the earth for a considerable time without becoming neutral. It proved that spray or vapour of hydrochloric acid had nothing whatever to do with producing the electrification, for these were absorbed by the water over which the gas was collected. It also suggested a possible means of measuring the difference of potential due to the contact of hydrogen with hydrochloric acid. After a few trials, however, I gave it up, and decided to determine the quantity by Sir W. Thomson's "Water-dropper."

A metal funnel with a long stem was fixed to the insulated plate, which was as usual connected to insulated quadrants. The funnel was filled with water, and a series of drops fell from the nozzle of the stem. The drops broke away at a distance of 6 or 7 inches from the body of the funnel. An *uninsulated* dish 3 inches in diameter, containing $\text{Zn} + \text{HCl}$, was placed under the nozzle, so that the drops fell into it. As the hydrogen passed into the air, enveloping the nozzle and falling drops, the spot moved rapidly up the scale to right and off it. I withdrew some of the charge from the needle,

and repeated the experiment. It again went off the scale. I withdrew a considerable quantity from the needle, and eventually reduced the sensibility of the instrument to such a degree that the deflexion never amounted to 300 divisions.

Fresh zinc and hydrochloric acid were now placed in the dish. The spot rapidly went up to 130 on the scale, from zero, and began to return. The "water-dropper" was then quickly disconnected from the quadrants, and the spot stood at 125. The dish was again supplied with fresh acid and zinc and placed in position, and when I could see by the fumes that the nozzle was enveloped in the escaping gas I again connected the quadrants to the "water-dropper," when the spot moved up the scale higher. This was repeated as long as the spot could be forced to go higher. At 187 from zero it only oscillated right and left to the extent of 3 or 5 divisions, but could not be forced higher by the liberation of hydrogen near the nozzle from fresh acid and zinc. I took this number as measuring the potential above earth of the gas as it escaped from the acid.

The reason for changing the acid so frequently is to be found in the fact, which I had already proved, that when hydrogen passes through a solution of ZnCl_2 it comes off with a negative charge; and on this account, if the measurement be not made when the gas is passing through at the first stage of the reaction, the result cannot be correct. And, indeed, no matter what precautions are taken the result must be a little too small.

Several preliminary experiments of this kind were made, and when I was satisfied that the result was definite and constant I made very carefully the three following determinations. In each case the acid was changed *nine* times:—

	Zero.	Deflexion.	Division.
(1)	362	552	190
(2)	359	544	185
(3)	358	545	187
			<hr/>
			3)562
			<hr/>
			187

I knew that I had reduced the sensibility of the electrometer very much, and when I proceeded to find the value of the scale-divisions in volts I found that the standard Daniell gave only a deflexion of from 3 to 6 divisions. Besides, this being very small I could not be certain of it to within a division, as the spot did not come precisely to zero. Of course,

I could not attempt to base a calculation on so uncertain a quantity.

To get over this little trouble I set up five Grove cells in series, which gave a deflexion either way of 40 scale-divisions.

Therefore,

$$\frac{187 \times 5}{40} = \text{D. P. in Grove cells.}$$

$$\frac{1.8 \times 18.7 \times 5}{4} = \text{D. P. in volts.}$$

$$42.08 = \text{D. P. in volts.}$$

The other numbers given were found in the same way. The potential of an electrified body depends on conditions, and the quantity I have determined may not be what I represent it. At all events, I have found approximately the potential above earth of a point in space immediately above the surface of the hydrochloric acid, through which hydrogen is passing. The distance between the surface of the acid and the drops where they broke away separately was 2 inches. If this distance were lessened another source of error would arise (or increase), for the particles of acid propelled by the hydrogen from the acid generator would strike the stem of the funnel and lessen the electrification, because, as has been proved, they are opposite in sign to the escaping gas.

But to return to my proposed straightforward experiment. I had intended to pass a current of neutral hydrogen through a column of strong hydrochloric acid, but found it impossible to neutralize the gas from a generator. However, I had now by trial become aware that a flask of hydrogen would become neutral after the lapse of some hours.

Three half Winchester quarts were filled with hydrogen by the displacement of water from a generator containing zinc and HCl, and were left during the night to lose their charges. At 8 o'clock the next morning one was uncorked and placed on the insulated plate. The hydrogen escaped, but the spot did not move. I was then pretty certain that the gas in the other two vessels was neutral.

A beaker, 7 inches high and 2 inches in diameter, was nearly filled with strong HCl, and a very slender delivery-tube, which had been attached to one of the vessels containing the hydrogen, was placed in it in such manner that any gas escaping from the vessel should pass right through a column of acid 6 inches high. An inverted metallic goblet was now attached to the insulated plate and quadrants, and placed in such position that any hydrogen issuing from the beaker con-

taining the acid should pass into it and be retained until it got into the air by diffusion. The hydrogen in the half Winchester quart was next forced through the acid by a stream of water. The spot did not move. No electrification was produced by the hydrogen bubbling through the acid. The experiment was repeated with the remaining half Winchester quart of hydrogen, but with the same result.

I had then to consider whether, in the face of this failure to electrify the neutral gas, I could reasonably stick to my theory of contact. I concluded that I could, and urge the following as sufficient grounds for my decision :—

I had proved beyond doubt that hydrogen holds a charge with amazing tenacity, and that it only gives it up when each molecule individually, it would appear, comes into contact with a conducting body. Such contacts were also proved to be most difficult to effect, and whatever difficulty exists in discharging the gas, by bringing it into contact with other substances, must also exist, and in a magnified form, when one tries to make contact between the gas and any substance for the purpose of charging. The difficulty of making real contact is not a new one. In fact, I hold that when the stream of hydrogen was forced through the pure acid, real contact was not made.

A very different state of things obtains when a piece of zinc is thrown into a quantity of acid. Here each molecule of hydrogen escapes from the chlorine into the acid separately, and very likely takes its charge while in the nascent condition. One cannot imitate the circumstances attending this condition of things by any possible arrangement of delivery-tubes, however small.

If it is proved that hydrogen or gases in general, in their nascent condition, take a charge when they come into contact with acids or solutions of salts, the fact, I should think, cannot fail to be of importance in the theory of the galvanic battery; and if it is proved that to make electrical contact between a gas and either metals or liquids is extremely difficult, what is known as “the air effect” in connexion with that theory appears to be negatived.

In conclusion, I wish to acknowledge the help in making many of the experiments which I have received from Messrs. Horsnell and Leach, students at present passing through the college.

St. Mary's College, Hammersmith,
November 1889.

VI. *The Effect of repeated Heating and Cooling on the Electrical Resistance of Iron.* By HERBERT TOMLINSON, F.R.S.*

SOME of the physical properties of iron wire, even if it has been previously well annealed, can be considerably modified by repeatedly raising the metal to the temperature of 100° C., and suffering it to cool again. The internal friction, for instance, of a torsionally oscillating iron wire can be largely and permanently reduced by this process. Again, in a paper quite recently presented to the Royal Society, the author has brought forward an instance of an iron wire, which when made to go through magnetic cycles of very minute range, alternately at the temperatures of 100° C. and 17° C., was found to be permanently reduced, both in its molecular friction and its magnetic permeability, at each heating and cooling to such an extent that ultimately the former of these two physical properties became one quarter, and the latter less than one half of their respective original amounts. The large diminution of permeability and friction was also attended by a considerable lessening of the *temporary* effects of change of temperature on these properties. The object of the present investigation was to ascertain whether the electrical resistance and temperature-coefficients of iron would also be altered by the heating and cooling process. According to Matthiessen the electrical resistance of metals can be expressed by the formula

$$R_t = R_0 (1 + at + bt^2),$$

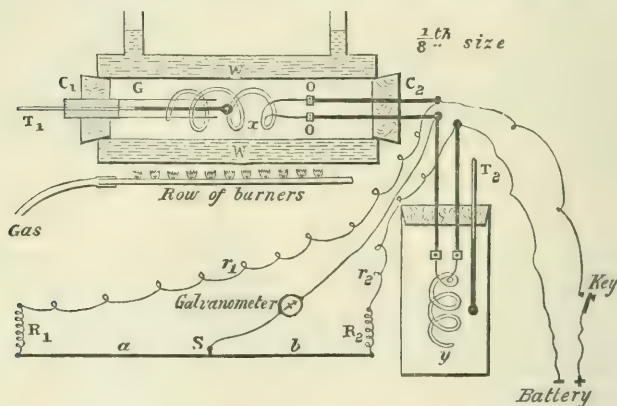
where R_t and R_0 are the resistances at t° and 0° C. respectively, and a and b are constants. For most pure metals the coefficient a is not very far from $\cdot 00366$, and the resistance varies, therefore, approximately as the absolute temperature; but with pure iron this coefficient is *much greater*. One of the questions which the inquiry was designed to answer was—Can the temperature-coefficient of iron be reduced by repeated heating and cooling to anything like $\cdot 00366$? This question has been answered in the negative, but, at the same time, it appears that the electrical resistance itself suffers a small but decided change.

The iron wire examined formed part of a hank supplied by

* Communicated by the Physical Society: read November 15, 1889.

The Author begs to acknowledge, with thanks, the assistance which he has received, in this and kindred investigations, from the "Elizabeth Thompson Science Fund."

Messrs. Johnson and Nephew, and was specially prepared and annealed for the author by these makers; it was again annealed by the author himself in the following manner:—The piece of iron wire, together with several others, was placed in an iron tube about 130 centim. long; the tube and its contents were then heated, in one of Fletcher's new tube-furnaces, to 1000°C . This high temperature was preserved for several hours, and the wires were then allowed to cool slowly in the furnace. The above operations were repeated on three different days, so that eventually the wire was probably annealed as well as it could be by the ordinary method. In order to avoid any appreciable effect from the earth's magnetic force, the furnace was placed in a direction at right angles to the magnetic meridian. After the annealing the wire, which was about 120 centim. long and 1 millim. in diameter, was wrapped round with strips of paper, and wound double in a coil 5 centim. in diameter and 12 centim. in length. It was then placed in an air-chamber consisting of two co-axial copper cylinders (see fig.) connected at their extremities, and enclosing between them an annular space filled with water. The whole arrangement is sufficiently shown in the figure.



In this figure *O O* are two clamps grooved so as to receive the ends of the iron wire *x**, the clamps themselves being soldered to stout copper connecting-rods; a German-silver wire, *y*, is similarly connected, and placed in a glass vessel.

* If the grooves, and the ends of the wire which fit into them, be well cleaned, clamping serves quite as well, for the purpose of connexion, as soldering, and is more convenient.

ab is a platinum-iridium wire of $\frac{1}{10}$ ohm resistance; R_2 is a resistance of 100 ohms, and R_1 a set of resistances from $\frac{1}{10}$ ohm to 200 ohms; the india-rubber-covered connecting-wires, r_1, r_2 , have each a resistance of $\frac{1}{20}$ ohm at the temperature of 17°C. ; and S is a sliding-piece which, by a suitable spring-and-catch arrangement, can be kept pressed on any part of ab . At the temperature of the room, the resistance of y is nearly equal to that of x , and R_1 as well as R_2 is nearly 100 ohms; consequently, any slight changes which may occur during the experimenting in the temperature of r_1, r_2 , and ab do not sensibly affect the balance. The thermometers T_1 and T_2 register the temperatures of x and y respectively*; T_1 has its bulb in the centre of x , and is enclosed by the glass tube G ; this tube is lined with india-rubber at the extremity outside the air-chamber, so that the thermometer can, if necessary for the purpose of reading, be pulled out to any required extent without causing any cooling; the glass tube and T_1 are both slightly slanted upwards to prevent the column of mercury from breaking when the temperature is falling.

For the purpose of preserving the temperature inside constant, the ends of the air-chamber are closed by corks, C_1, C_2 , and the vacant spaces inside are stuffed with cotton-wool (not shown in the figure). The water in the annular space W is heated by a row of burners, made by piercing pin-holes at equal intervals in a copper tube, closed at one end, and connected at the other with the gas. By adjusting the supply of gas or by altering the distance of the row of burners from the air-chamber, any required temperature up to 100°C. could be maintained nearly, if not quite, constant for a considerable length of time. In 15 minutes the water could be raised to 100°C. ; and then, by diminishing the supply of gas so that the water only just boiled, this temperature could be kept up for 16 hours without adding more water; when it was necessary to maintain the temperature at 100°C. for longer periods of time, the vessel was replenished with boiling water.

It will be seen from the figure that there is a "Wheatstone's Bridge" arrangement for determining the resistance-ratio, $x : y$. The temperature of y varied by only a few degrees during the whole of the inquiry; and as both the actual resist-

* Only one thermometer was used for T_1 in this particular investigation, but the author generally employs, in work of this kind, three thermometers in turn. One of these thermometers is graduated from -5°C. to 30°C. , the second from 30°C. to 65°C. , and the third from 65°C. to 100°C. ; all three thermometers are divided into tenth degrees, and have been carefully compared with the Kew standards.

ance of the coil at 17° C. and its temperature-coefficient were known, the resistance of y at any other temperature could be calculated.

It is usual in experiments with the "bridge" to close first the battery-circuit, and immediately afterwards that of the galvanometer; but the author prefers to keep the galvanometer-circuit always closed, and to observe the effect of closing the battery-circuit. It is true that in the latter case there is always a momentary throw of the needle due to self-induction in the wires, but this, with the arrangement shown above, is very slight; and with no more delay than that of two or three seconds, it can be easily ascertained whether the act of closing the battery-circuit causes *any alteration in the difference of potential at the galvanometer-terminals**. If, on the contrary, the former of the two methods be employed, there arises more or less inaccuracy from the presence of thermo-electrical currents set up in one or more branches of the bridge by slight variations in the temperature of the air at different parts of the room. Besides, even if the air could be maintained at perfectly uniform temperature throughout, thermo-electrical currents are always produced by the act of pressing down the sliding-piece, S, on the wire ab , and by Peltier effects.

The act of bending the wire into the form of the coil produced, as might be expected, a slight permanent change in its resistance, which was thereby increased by $\frac{1}{4}$ per cent.; doubtless a portion, but only a small one, of the whole reduction of resistance, to be presently recorded, is to be attributed to the partial or complete removal of the effect of coiling.

When everything was ready, and the wire had been left undisturbed for several hours, its resistance and temperature were determined; the latter was then raised to 100° C., or very nearly to 100° C., and maintained thereat for at least 8 hours†; and during this period the resistance of the wire was tested several times. The wire was then permitted to cool down, and its resistance was again determined about 16 hours afterwards. The same operations were repeated again and again, until the metal showed that no sensible change of resistance was produced by the heating and cooling. The results are given in the following Table:—

* There is always a difference of potential at the galvanometer-terminals arising from thermo-electrical effects; see what follows.

† The deviation from 100° C. never exceeded $\frac{3}{10}^{\circ}$ C., and could in all cases be accounted for by changes in the barometric pressure.

Number of times heated to 100° C.	Specific resistance in O.G.S. units at 17° C. R_{17} .	Differences between consecutive values of R_{17} .	Specific resistance at 100° C. R_{100} .	$R_{100} - R_{17}$ *.	$\frac{R_{100} - R_{17}}{R_{17}}$ *.	Remarks.
0	11162					
1	10942	220	16029	4952	·4527	{ Kept at 100° C. for 8 hours; the battery-current always applied in the same direction.
2	10807	135	15796	4922	·4526	
3	10772	35	15789	4985	·4613	
4	10757	15	15747	4999	·4633	Ditto.
5	10755	2	4996	·4638	Ditto.
6	10727	28	15724	{ Kept at 100° C. for 26 hours; the battery-current applied first in one direction and then in the opposite.
7	10711	16	15679	4983	·4629	
8	10694	17	15674	4965	·4636	
9	10689	5	Ditto.
10	15654	Ditto.
11	Ditto.
12	10688	Ditto.

* For the mode of calculating the numbers in these columns, see what follows.

It will be noticed that the specific resistance both at 17° C. and at 100° C. is diminished with each repetition of the heating and cooling process, until, finally, it becomes about $4\frac{1}{2}$ per cent. less than at first. Thus, though the permanent effect on the electrical resistance is very much less than that on the permeability for very minute magnetizing forces, it is quite sensible.

At the sixth heating the wire was kept at 100° C. for 26 hours and, moreover, the battery-current was applied first in one direction and then in the opposite. These reversals of the current served to increase the rate of diminution of the resistance.

The maintaining the temperature at 100° C. for 26 hours did not diminish the resistance as much as the next two heatings and coolings taken together; evidently, therefore, the cooling exerts an influence as well as the heating. It is not, in fact, of much use prolonging each period of heating beyond 8 hours, whilst, on the contrary, a less time will hardly suffice, heating and cooling in rapid alternation being comparatively ineffectual.

Though the specific resistance of the annealed iron is permanently diminished by the heating and cooling process, this is not so with the *temporary* change of resistance arising from change of temperature; the sixth column of the Table shows that the temporary increase of resistance produced by raising the temperature from 17° C. to 100° C. is not affected by the heating and cooling process, whilst the temporary increase of resistance *per unit* becomes greater in proportion as the specific resistance itself becomes less.

The values of $R_{100} - R_{17}$ and $\frac{R_{100} - R_{17}}{R_{17}}$ were calculated so as to avoid, as much as possible, error arising from the *permanent* changes consequent on the heating and cooling. Let C_1, C_2, C_3 , &c., represent the resistances of the cold wire after the first, second, third, &c., heatings, and H_1, H_2, H_3 , &c., the corresponding resistances of the hot wire, then the numbers in the sixth column were obtained from $\frac{H_1 + H_2}{2} - C_1$, $H_2 - \frac{C_1 + C_2}{2}$, $\frac{H_2 + H_3}{2} - C_3$, $H_3 - \frac{C_3 + C_4}{2}$, &c., and those in the last column by dividing these by C_1 , $\frac{C_1 + C_2}{2}$, C_3 , $\frac{C_3 + C_4}{2}$, &c., respectively. Of course, the temperature of the room was not always 17° C., but the resistance of x at 17° C. could be calculated from its actual resistance at the temperature

at the time by means of a formula ultimately obtained for the resistance of the wire at any temperature*. This formula was calculated from the results of a number of very careful observations at 17° C., 60° C., and 100° C., and after the heating and cooling process had ceased to affect the resistance. The formula thus obtained was :—

$$R_t = R_0 (1 + \cdot 005131 t + \cdot 00000815 t^2);$$

whilst the formula deducible from Matthiessen's results for *pure* iron annealed in hydrogen is

$$R_t = R_0 (1 + \cdot 005425 t + \cdot 0000083 t^2).$$

The specific resistance at 0° C. ($R_{0\cdot T}$) of the author's iron was 9808 electromagnetic units, whilst that of Matthiessen's pure iron ($R_{0\cdot M}$) is given on the authority of the late Prof. Jenkin as 9718†. It seems not improbable that this last value is from 4 to 5 per cent. too high; for it follows from Matthiessen's researches that the resistances at any temperature of a pure metal and its alloy should be in the inverse ratio of the rates of increase of resistance at that temperature, so that

$$\frac{R_{0\cdot M}}{R_{0\cdot T}} \text{ should equal } \frac{\cdot 005131}{\cdot 005425},$$

which, if the author's result be assumed to be correct, would make $R_{0\cdot M}$ equal to 9277.

Unfortunately, Matthiessen did not determine the *absolute* resistance of iron and many of the other pure metals examined by him, and it appears from Prof. Jenkin's own statement‡ that the calculated results for these metals cannot be depended on for any great degree of accuracy. The author, therefore, ventures to express the hope that the B. A. Electrical Standards Committee may be induced to determine the absolute resistances and the temperature-coefficients of those of the pure metals which are in ordinary use.

* Similarly for the higher temperature of 100° C.

† The number actually given by Prof. Jenkin has been multiplied by ·9889 (the value of the B.A. unit in terms of the legal ohm).

‡ See note on p. 250 of Prof. Jenkin's book on 'Electricity and Magnetism.'

VII. *On the Importance of Quaternions in Physics.**By Professor TAIT*.*

MY subject may usefully be treated under three heads, viz.:—

1. The importance of mathematics, in general, to the progress of physics.

2. The special characteristics required to qualify a calculus for physical applications.

3. How quaternions meet these requirements.

The question has often been asked, and frequently answered (one way or other) in the most decided manner:—Whether is experiment or mathematics the more important to the progress of physics? To any one who really knows the subject, such a question is simply absurd. You might almost as well ask:—Whether is oxygen or hydrogen the more necessary to the formation of water? Alone, either experiment or mathematics is comparatively helpless:—to their combined or alternate assaults everything penetrable must, some day, give up its secrets.

To take but one instance, stated as concisely as possible:—think of the succession of chief steps by which Electromagnetism has been developed. You had first the fundamental experiment of Oersted:—next, the splendid mathematical work of Ampère, which led to the building up of a magnet of any assigned description by properly coiling a conducting wire. But experiment was again required, to solve the converse problem:—and it was by one of Faraday's most brilliant discoveries that we learned how, starting with a magnet, to produce an electric current. Next came Joule and v. Helmholtz to show (the one by experiment, the other by analysis) the source of the energy of the current thus produced:—in the now-a-days familiar language, why a powerful engine is required to drive a dynamo. Passing over a mass of important contributions mathematical and experimental, due to Poisson, Green, Gauss, Weber, Thomson, &c., which, treated from our present point of view, would furnish a narrative of extraordinary interest, we come to Faraday's *Lines of Force*. These were suggested to him by a long and patient series of experiments, but conceived and described by him in a form requiring only technical expression to become fully mathematical in the most exclusive sense of the word. This

* Abstract of an Address to the Physical Society of the University of Edinburgh, November 14, 1889. See the Author's Address to Section A at the British Association, 1871.

technical expression was given by Clerk-Maxwell in one of his early papers, which is still in the highest degree interesting, not only as the first step to his *Theory of the Electromagnetic Field*, but as giving by an exceedingly simple analogy the physical interpretation of his equations. Next, the narrative should go back to the establishment of the Wave-theory of Light:—to the mathematics of Young and Fresnel, and the experiments of Fizeau and Foucault. Maxwell's theory had assigned the speed of electromagnetic waves in terms of electrical quantities to be found by experiment. The close agreement of the speed, so calculated, with that of light rendered it certain that light is an electromagnetic phenomenon. But it was desirable to have special proof that there can be electromagnetic waves: and to measure the speed of propagation of such as we can produce. Here experiment was again required, and you all know how effectively it has just been carried out by Hertz. It is particularly to be noticed that the more important experimental steps were, almost invariably, suggested by theory—that is, by mathematical reasoning of some kind, whether technically expressed or not. Without such guidance experiment can never rise above a mere groping in the dark.

I have to deal, at present, solely with the mathematical aspect of physics; but I have led up to it by showing its inseparable connexion with the experimental side, and the consequent necessity that every formula we employ should as openly as possible proclaim its physical meaning. In presence of this necessity we must be prepared to forego, if required, all lesser considerations, not excluding even such exceedingly desirable qualities as compactness and elegance. But if we can find a language which secures these to an unparalleled extent, and at the same time is transcendently expressive—bearing its full meaning on its face—it is surely foolish at least not to make habitual use of it. Such a language is that of Quaternions; and it is particularly noteworthy that it was invented by one of the most brilliant Analysts the world has yet seen, a man who had for years revelled in floods of symbols rivalling the most formidable combinations of Lagrange, Abel, or Jacobi. For him the most complex trains of formulae, of the most artificial kind, had no secrets:—he was one of the very few who could afford to dispense with simplifications: yet, when he had tried quaternions, he threw over all other methods in their favour, devoting almost exclusively to their development the last twenty years of an exceedingly active life.

Everyone has heard the somewhat peculiar, and more than

doubtful, assertion—*Summum jus, summa injuria*. We may, without any hesitation, make a parallel but more easily admitted statement:—*The highest art is the absence* (not, as Horace would have it, the concealment) *of artifice*. This commends itself to reason as well as to experience; but nowhere more forcibly than in the application of mathematics to physical science. The difficulties of physics are sufficiently great, in themselves, to tax the highest resources of human intellect; to mix them up with avoidable mathematical difficulties is unreason little short of crime. [To be obliged to evaluate a definite integral, or to solve a differential equation, is a necessity of an unpleasant kind, akin to the enforced extraction of a cube root; and here artifice is often requisite in our present state of ignorance: but its introduction for such purposes is laudable. It does for us the same kind of service which has been volunteered in the patient labour of the calculators of logarithmic tables. It is not of inevitable, but of gratuitous, complications that we are entitled to complain.] The intensely artificial system of Cartesian coordinates, splendidly useful as it was *in its day*, is one of the wholly avoidable encumbrances which now retard the progress of mathematical physics. Let any of you take up a treatise on the higher branches of hydrokinetics, or of stresses and strains, and then let him examine the twofold notation in Maxwell's 'Electricity.' He will see at a glance how much expressiveness as well as simplicity is secured by an adoption of the mere notation, as distinguished from the processes, of quaternions. It is not difficult to explain the cause of this. But let us first take an analogy from ordinary life, which will be found to illustrate fairly enough some at least of the more obvious advantages of quaternions.

There are occasions (happily rare) on which a man is required to specify his name in full, his age, height, weight, place of birth, family history, character, &c. He may be an applicant for a post of some kind, or for a Life Policy, &c. But it would be absolutely intolerable even to mention him, if we had invariably to describe him by recapitulating all these particulars. They will be forthcoming when wanted; but we must have, for ordinary use, some simple, handy, and unambiguous method of denoting him. When we wish to deal with any of his physical or moral qualities, we can easily do so, because the short specification which we adopt in speaking of him is sufficient for his identification. It *includes* all his qualities. We all recognize and practise this in ordinary life; why should we outrage common-sense by doing something very different when we are dealing with scientific matters, especially

in a science such as mathematics, which is purely an outcome of logic?

In quaternions, a calculus uniquely adapted to Euclidian space, this entire freedom from artifice and its inevitable complications is the chief feature. The position of a point (relative of course to some assumed origin) is denoted by a single symbol, which *fully* characterizes it, and depends upon length and direction alone, involving no reference whatever to special coordinates*. Thus we use ρ (say) in place of the Cartesian x, y, z , which are themselves dependent, for their numerical values, upon the particular scaffolding which we choose to erect as a (temporary) system of axes of reference. The distance between two points is

$$T(\rho - \rho'),$$

instead of the cumbrous Cartesian

$$\{(x - x')^2 + (y - y')^2 + (z - z')^2\}^{\frac{1}{2}}.$$

But the distance in question is fully symbolized as to direction as well as length by the simple form

$$\rho - \rho'.$$

If three conterminous edges of a parallelepiped be ρ, ρ', ρ'' , its volume is

$$-S. \rho \rho' \rho''.$$

Even when advantage is taken of the remarkable condensation secured by the intensely artificial notation for determinants, Cartesian methods must content themselves with the much more cumbrous expression

$$\begin{vmatrix} x & y & z \\ x' & y' & z' \\ x'' & y'' & z'' \end{vmatrix}.$$

As we advance to higher matters, the Cartesian complexity tells more and more; while quaternions preserve their simplicity. Thus any central surface of the second degree is expressible by

$$S\rho\phi\rho = -1, \quad \text{or} \quad T\phi^{\frac{1}{2}}\rho = 1;$$

while the Cartesian form develops into

$$Ax^2 + 2B''xy + A'y^2 + 2B'xz + 2Byz + A''z^2 = 1.$$

The homogeneous strain which changes ρ into ρ' is expressible

* Note here that though absolute *position* is an idea too absurd even for the majority of metaphysicians, absolute *direction* is a perfectly definite physical idea. It is one essential part of the first law of motion.

by a single letter :—thus

$$\rho' = \psi \rho.$$

Its Cartesian form requires three equations,

$$x' = ax + by + cz,$$

$$y' = dx + ey + fz,$$

$$z' = gx + hy + iz.$$

These may be simplified, but only a little, by employing the notation for a matrix. To express in quaternions the conjugate strain, a mere dash is required : thus

$$\psi';$$

while with the artificial scaffolding we must write our three equations again, arranging the coefficients as below :—

$$\begin{array}{ccc} a & d & g \\ b & e & h \\ c & f & i. \end{array}$$

If we now ask the question, What strain will convert the ellipsoid above into the unit sphere, the answer will be some time in coming from the ponderous Cartesian formulæ. The quaternion formula assigns it at once as $\phi^{\frac{1}{3}}$.

When Gauss gave his remarkable expression for the number of interlinkings of two endless curves in space, he had to print it as

$$\frac{1}{4\pi} \iint \frac{(x' - x)(dy dz' - dz dy') + (y' - y)(dz dx' - dx dz') + (z' - z)(dx dy' - dy dx')}{\{(x' - x)^2 + (y' - y)^2 + (z' - z)^2\}^{\frac{3}{2}}}.$$

What an immense gain in simplicity and intelligibility is secured when we are enabled to write this in the form

$$-\frac{1}{4\pi} \iint \frac{\mathbf{S} \cdot \overline{\rho - \rho_1} d\rho d\rho_1}{T_{\rho - \rho_1}^3};$$

or as

$$\frac{1}{4\pi} \int \mathbf{S} \cdot d\rho \int \frac{\mathbf{V} \overline{\rho - \rho_1} d\rho_1}{T_{\rho - \rho_1}^3};$$

so that we instantly recognize in the latter factor the vector force exerted by unit current, circulating in one of the closed curves, upon a unit pole placed anywhere on the other; and thus see that the whole integral represents the work required to carry the pole once round its circuit.

Without as yet defining ∇ , I shall take, as my final example, one in which it is involved. A very simple term,

which occurs in connexion with the strain produced by a given displacement of every point of a medium, is

$$S\alpha\nabla \cdot S\beta\nabla_1 \cdot V\sigma\sigma_1.$$

Its Cartesian expression is, with the necessary specification

$$\sigma = i\xi + j\eta + k\zeta,$$

made up of three similar terms of which it is sufficient to write one only, viz.,

$$(ab' - ba')\left(\frac{d\eta}{dx} \frac{d\xi}{dy} - \frac{d\eta}{dy} \frac{d\xi}{dx}\right) + (ca' - ac')\left(\frac{d\eta}{dz} \frac{d\xi}{dx} - \frac{d\eta}{dx} \frac{d\xi}{dz}\right) \\ + (bc' - cb')\left(\frac{d\eta}{dy} \frac{d\xi}{dz} - \frac{d\eta}{dz} \frac{d\xi}{dy}\right).$$

Now, suppose this to be given as the x -coordinate of a point, similar expressions (formed by cyclical permutation) being written for the y and z coordinates. How long would it take you to interpret its meaning?

Look again at the quaternion form, and you see at a glance that it may be written

$$V(S\alpha\nabla \cdot \sigma)(S\beta\nabla_1 \cdot \sigma),$$

in which its physical meaning is more obvious than any mere form of words could make it.

Or you may at once transform it to

$$-\frac{1}{2}S \cdot (V\alpha\beta) \nabla\nabla_1 \cdot V\sigma\sigma_1,$$

which shows clearly why it vanishes when α and β are parallel.

I need not give more complex examples :—because, though their quaternion form may be simple enough (containing, say, 8 or 10 symbols altogether), even this unusually large blackboard would not suffice to exhibit more than a fraction of the equivalent Cartesian form.

Any mathematical method, which is to be applied to physical problems, must be capable of expressing not only space-relations but also the grand characteristics (so far as we yet know them) of the materials of the physical world. I have just briefly shown how exactly and uniquely quaternions are adapted to Euclidian space; we must next enquire how they meet the other requirements.

The grand characteristics of the physical world are :—Conservation of Matter, with absolute preservation of its identity; and Conservation of Energy, in spite of perpetual change of a character such as entirely to prevent the recognition of identity. The first of these is very simple, and needs no preliminary remarks. But the methods of symbolizing

change are almost as numerous as are the various kinds of change. The more important of them employ forms of the letter *D* :—viz. *d*, *∂*, *D*, *Δ*, *δ*, and *∇*.

From our present point of view little need be said of *Δ*, which is the equivalent of (*D*—1) or of ($\epsilon^{d/dx} - 1$), because the changes which it indicates take place by starts and not continuously. Good examples of problems in which it is required are furnished by the successive rebounds of a ball from a plane on which it falls, or by the motion of a light string, loaded at intervals with pellets.

Various modes of applying the symbol *d* are exemplified in the equation

$$dQ = \left(\frac{dQ}{dx}\right)dx + \left(\frac{dQ}{dy}\right)dy + \left(\frac{dQ}{dz}\right)dz.$$

In the terms *dx*, *dy*, *dz*, the symbol *d* stands for changes of value (usually small) of quantities treated as independent. In the term *dQ* it stands for the whole consequent change of a quantity which is a function of these independents. By the factors $\left(\frac{dQ}{dx}\right)$ &c. we represent the *rates* of increase of *Q*,

per unit of length, in the directions in which *x*, *y*, *z* are respectively measured. The contrast between the native simplicity of the left-hand, and the elaborate artificiality of the right-hand, member of the equation, shows at once the need for improvement. To express the rate of change per unit of length in any other direction, we have to adopt the cumbrous expedient of introducing *three* direction-cosines, and the result is given in the form

$$l \frac{dQ}{dx} + m \frac{dQ}{dy} + n \frac{dQ}{dz}.$$

The above equation may be read as pointing out, *at any one instant*, how a function of position varies from point to point. To express the change, *at any one place*, from one instant to the next, we write in the usual notation

$$dQ = \left(\frac{dQ}{dt}\right)dt.$$

But if we have to express the changes, from instant to instant, of some property of a point, which is itself subject to an assigned change of position with time, we have to combine these expressions, and to indicate the relation of position to time. Thus we build up the complicated expression

$$dQ = \left(\frac{dQ}{dt}\right)dt + \left(\frac{dQ}{dx}\right)\frac{dx}{dt}dt + \left(\frac{dQ}{dy}\right)\frac{dy}{dt}dt + \left(\frac{dQ}{dz}\right)\frac{dz}{dt}dt.$$

Here the symbol δ is called in, to effect a slight simplification; and we go a little further in the same direction by putting u, v, w for

$$\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt},$$

which are obviously the components of velocity of the point for which Q is expressed. Thus we write

$$\frac{\partial Q}{\partial t} = \left(\frac{dQ}{dt}\right) + u\left(\frac{dQ}{dx}\right) + v\left(\frac{dQ}{dy}\right) + w\left(\frac{dQ}{dz}\right).$$

Of course you all know this quite well; and you may ask why I thus enlarge upon it. It is to show you how completely artificial and unnatural are our recognized modes of expression.

Fresnel well said :—*La nature ne s'est pas embarrassée des difficultés d'analyse, elle n'a érité que la complication des moyens.* Why should we not attempt, at least, to imitate nature by seeking simplicity?

The notation δ , as commonly used, is (like the d in dQ above) quite unobjectionable. At least we cannot see how to simplify it further. Its effect is to substitute, for any one point of a figure or group, a proximate point in space, so that the figure or group of points undergoes slight, and generally continuous, but otherwise wholly arbitrary displacement and distortion. It thus appears that d and δ are entitled to take their places in a calculus, such as quaternions, where simplicity, naturalness, and direct intelligibility are the chief qualities sought. We have now to inquire how such expressions as

$$l \frac{dQ}{dx} + m \frac{dQ}{dy} + n \frac{dQ}{dz}$$

can be put in a form in which they will bear their meaning on their face.

It was for this purpose that Hamilton introduced his symbol ∇ . No doubt, it was originally defined in the cumbrous and unnatural form

$$i \frac{d}{dx} + j \frac{d}{dy} + k \frac{d}{dz}.$$

But that was in the very infancy of the new calculus, before its inventor had succeeded in completely removing from its formulæ the fragments of their Cartesian shell, which were still persistently clinging about them. To be able to speak freely about this remarkable operator, we must have a name

attached to it, and I shall speak of it as *Nabla**. We may define it in many ways, all independent of any system of coordinates. Thus we may give the definition

$$-S\alpha\nabla = d_\alpha,$$

meaning that, whatever unit-vector α may be, the resolved part of ∇ parallel to that line gives the rate of increase of a function, per unit of length, along it. From this we recover, at once, Hamilton's original definition:—thus

$$\nabla = -\alpha S\alpha\nabla - \beta S\beta\nabla - \gamma S\gamma\nabla = \alpha d_\alpha + \beta d_\beta + \gamma d_\gamma,$$

α, β, γ being *any* system of mutually rectangular unit-vectors.

But, preferably, we may define *Nabla* once for all by the equation

$$-Sd\rho\nabla = d,$$

where d has the meaning already assigned. The very nature of these forms shows at once that *Nabla* is an *Invariant*, and therefore that it ought not to be defined with reference to any system of coordinates whatever.

Either of the above definitions, however, shows at once that the effect of applying ∇ to any scalar function of position is to give its *vector-rate of most rapid change*, per unit of length.

Hence, when it is applied to a potential, it gives in direction and magnitude the force on unit mass; while from a velocity-potential it derives the vector velocity. From the temperature, or the electric potential, in a conducting body we get (employing the corresponding conductivity as a numerical factor) the vector flux of heat or of electricity. Finally, when applied to the left-hand member of the equation of a series of surfaces

$$u = C,$$

it gives the reciprocal of the shortest vector distance from any point of one of the surfaces to the next; what Hamilton called the vector of proximity.

If we form the square of *Nabla* directly from Hamilton's original definition, we find

$$\nabla^2 = - \left\{ \left(\frac{d}{dx} \right)^2 + \left(\frac{d}{dy} \right)^2 + \left(\frac{d}{dz} \right)^2 \right\},$$

* Hamilton did not, so far as I know, suggest any name. Clerk-Maxwell was deterred by their vernacular signification, usually ludicrous, from employing such otherwise appropriate terms as *Sloper* or *Grader*; but adopted the word *Nabla*, suggested by Robertson Smith from the resemblance of ∇ to an ancient Assyrian harp of that name.

simply the negative of what has been called Laplace's Operator :—that which derives from a potential the corresponding distribution of matter, electricity, &c.

Thus Laplace's equation for spherical harmonics &c. is merely

$$\nabla^2 u = 0 ;$$

and, as $1/T(\rho - \alpha)$ is evidently a special integral, an indefinite series of others can be formed from it by operating with scalar functions of ∇ , which are commutative with ∇ , such as $S\beta\nabla$, $\epsilon^{-s\gamma\nabla}$, &c. In passing, we may remark that if β be a unit vector, $il + jm + kn$, we have

$$-S\beta\nabla = l \frac{d}{dx} + m \frac{d}{dy} + n \frac{d}{dz}.$$

This is the answer to the question proposed a little ago.

The geometrical applications of Nabla do not belong to my subject, and they have been very fully given by Hamilton. But, for its applications to physical problems, certain fundamental theorems are required, of which I will take only three of the more important ;—an analytical, a kinematical, and a physical one.

I. The analytical theorem is very simple, but it has most important bearings upon change of independent variables, and other allied questions in tridimensional space. Few of you, without the aid of quaternions or of immediately previous preparation, would promptly transform the independent variables in a partial differential equation from x, y, z to r, θ, ϕ :—and you would certainly require some time to recover the expressions in generalized (orthogonal) coordinates. But Nabla does it at once. Thus, let

$$\nabla_\sigma = i \frac{d}{d\xi} + j \frac{d}{d\eta} + k \frac{d}{d\zeta},$$

where

$$\sigma = i\xi + j\eta + k\zeta,$$

ξ, η, ζ being any assigned functions of x, y, z . Further, let

$$d\sigma = \phi d\rho,$$

where ϕ , in consequence of the above data, is a definite linear and vector function. Then, from the mere definition of Nabla,

$$Sd\sigma\nabla_\sigma = -d = Sd\rho\nabla,$$

which gives at once

$$S \cdot \phi d\rho \nabla_\sigma = S \cdot d\rho \phi' \nabla_\sigma = Sd\rho \nabla.$$

As $d\rho$ may have absolutely any direction, this is equivalent to

$$\phi' \nabla \sigma = \nabla,$$

where ϕ' is the conjugate of ϕ .

II. The fundamental kinematical theorem is easily obtained from the consideration of the continuous displacement of the points of a fluid mass. (It is implied in the word "continuous" that there is neither rupture nor finite sliding.)

If σ be the displacement of the point originally at ρ , that of $\rho + d\rho$ is

$$\sigma + d\sigma = \sigma - S d\rho \nabla \cdot \sigma;$$

and thus the strain, in the immediate neighbourhood of the point ρ , is such as to convert $d\rho$ into

$$d\rho - S d\rho \nabla \cdot \sigma.$$

Thus the strain-function is

$$\psi \tau = \tau - S \tau \nabla \cdot \sigma.$$

If this correspond to a linear dilatation e , and a vector-rotation ϵ , both being quantities whose squares are negligible, we must have

$$\psi \tau = (1 + e) \tau + V \epsilon \tau.$$

Comparing, we have

$$-S \tau \nabla \cdot \sigma = e \tau + V \epsilon \tau,$$

from which at once (by taking the sum for any three directions at right angles to one another),

$$\nabla \sigma = -\Sigma(e) + 2\epsilon;$$

so that

$$S \nabla \sigma \text{ represents the compression,}$$

and

$$\frac{1}{2} V \nabla \sigma \quad \text{,,} \quad \text{,,} \quad \text{vector-rotation,}$$

of the element surrounding ρ .

By the help of these expressions we easily obtain the stress-function for a homogeneous isotropic solid, in terms of the displacement of each point, in the form

$$\phi \omega = -n(S \omega \nabla \cdot \sigma + \nabla S \omega \sigma) - (c - \frac{2}{3}n) \omega S \nabla \sigma;$$

where n and c are, respectively, the rigidity and the resistance to compression; and $\phi \omega$ is the stress, per unit of surface, on a plane whose unit normal is ω .

III. The fundamental physical relation is that expressing conservation of matter, commonly called the equation of continuity. We have only to express symbolically that the increase of mass in a finite simply-connected space, due to a displacement, is the excess of what enters over what leaves the

space. This gives at once

$$\iiint S \nabla \sigma ds = \iint S U \nu \sigma ds,$$

where $U \nu$ is unit normal drawn *outwards* from the bounding surface. If we put for σ the expression $u \nabla v$, where u and v are any two scalar functions of position, this becomes Green's Theorem.

If the space considered be imagined as bounded by two indefinitely close *parallel* surfaces, and by the normals at each point of a closed curve drawn on one of them, this is easily reduced to the form of the line and surface integral

$$\iint S . U \nu \nabla \sigma ds = \int S \sigma d\rho.$$

The simplest forms of these equations are respectively

$$\iiint \nabla u ds = \iint U \nu u ds,$$

and

$$\iint V (U \nu \nabla) u ds = \int d\rho u,$$

where u is any scalar function of position. But it is clear from the mode in which it enters that u may be any quaternion. And it is easy to build on these an indefinite series of more complex relations. Thus, for instance, if σ and τ be any two vector-functions of ρ , we have

$$\iiint (\sigma \nabla^2 \tau + K \nabla \sigma . \nabla \tau) ds = \iint \sigma U \nu \nabla \tau ds,$$

which has many important transformations. You will find it laborious, but alike impressive and instructive, to write this simple formula in Cartesian coordinates. It consists of four separate equations, containing among them 189 terms in all!

In the three relations just given we have the means of applying quaternions to various important branches of mathematical physics, where Nabla is indispensable. But I must confine myself to one example, so I will take very briefly the equations of fluid motion.

Let e be the density, and σ the vector-velocity, at the point ρ in a fluid. Consider the rate at which the density of a little portion of the fluid at ρ increases as it moves along. We have at once, for the equation of continuity,

$$\frac{\partial e}{\partial t} = e S \nabla \sigma ;$$

which we may write, if we please, as

$$\frac{de}{dt} = S \nabla (e \sigma).$$

This is the result we should have obtained if we had considered the change of contents of a *fixed* unit volume in space. Next consider the rate at which the element gains momentum as it proceeds. We write at once, since momentum cannot originate or be destroyed by processes *inside* the element,

$$e \frac{\partial \sigma}{\partial t} = -e \nabla P + \iiint \phi U \nu ds,$$

where P is the potential energy of unit mass at ρ , and $\phi U \nu$ is the stress-function due to pressure and viscosity. We have already had the form of this function; so that the equation transforms at once into

$$e \frac{\partial \sigma}{\partial t} = -e \nabla P - \nabla p - n(\nabla^2 \sigma + \frac{1}{3} \nabla S \nabla \sigma);$$

which contains the three ordinarily given equations. Here n is the coefficient of viscosity, and the pressure p enters the equation in the form

$$e S \nabla \sigma.$$

To obtain v. Helmholtz's result as to vortex-motion, put $n=0$, and we deduce for the rate of change of vector-rotation of an element, as it swims along,

$$\frac{\partial}{\partial t} V \nabla \sigma = V \cdot \nabla V \cdot \sigma V \nabla_1 \sigma_1.$$

If the fluid be incompressible, this becomes

$$\frac{\partial}{\partial t} V \nabla \sigma = -S \cdot \nabla_1 \sigma_1 \nabla \cdot \sigma.$$

From either it is obvious that the rate of change of the vector-rotation vanishes where there is no rotation. But time forbids any further discussion of formulæ.

Hydrokinetics, as presented by Lagrange and Cauchy, was rather a triumph of mathematical skill than an inviting or instructive subject for the student. The higher parts of it were wrapped up in equations of great elegance, but of almost impenetrable meaning. They were first interpreted, within the memory of some of us, by Stokes and v. Helmholtz, after we know not what amount of intellectual toil. The magnificent artificers of the earlier part of the century were, in many cases, blinded by the exquisite products of their own art. To Fourier, and more especially to Poincot, we are indebted for the practical teaching that a mathematical formula, however brief and elegant, is merely a step towards knowledge, and an all but useless one, until we can thoroughly read its meaning. It may in fact be said with truth that we

are already in possession of mathematical methods, of the artificial kind, fully sufficient for all our present, and at least our immediately prospective, wants. What is required for physics is that we should be enabled at every step to feel intuitively what we are doing. Till we have banished artifice we are not entitled to hope for full success in such an undertaking. That Lagrange and Cauchy missed the import of their formulæ, leaving them to be interpreted some half-century later, is merely a case of retributive justice:—

“... neque enim lex aequior ulla
Quam necis artifices arte perire suâ.”

Lagrange in the preface to that wonderful book, the *Mécanique Analytique*, says:—

“Les methodes que j’y expose ne demandent ni constructions, ni raisonnemens géométriques ou mécaniques, mais seulement des opérations algébriques, assujéties à une marche régulière et uniforme.”

But note how different is Poinso't's view:—

“Gardons-nous de croire qu’une science soit faite quand on l’a réduite à des formules analytiques. Rien ne nous dispense d’étudier les choses en elles-mêmes, et de nous bien rendre compte des idées qui font l’objet de nos spéculations.”

No one can doubt that, in this matter, the opinion of the less famous man is the sound one. But Poinso't's remark must be confined to the analytical formulæ known to him. For it is certain that one of the chief values of quaternions is precisely this:—that no figure, nor even model, can be more expressive or intelligible than a quaternion equation.

VIII. *An Approximate Algebraic Expression of the Periodic Law of the Chemical Elements.* By THOS. CARNELLEY, D.Sc., Professor of Chemistry in the University of Aberdeen.*

[Plate I.]

SEVERAL attempts have of late years been made to express the atomic weights of the Elements by algebraic formulæ. Of these that of Dr. E. J. Mills (*Phil. Mag.* [5] xviii. p. 393; xxi. p. 151) expresses the atomic weights by a logarithmic function

$$15(p - 0.9375^t),$$

in which p and t are whole numbers.

Another attempt, referred to by Prof. Mendeljeff in his

* Communicated by the Author.

Phil. Mag. S. 5. Vol. 29. No. 176. Jan. 1890.

H

Faraday Lecture of this year (Chem. Soc. Journ. iv. p. 642) as having been made by Tchitchérin in 1888, seeks to express the relations between the atomic volumes of the alkaline metals by the formula $A(2 - 0.00535 An)$, where A = the atomic weight and $n = 8$ for Li and Na, 4 for K, 3 for Rb, and 2 for Cs.

In a paper read at the Aberdeen Meeting of the British Association in 1885 (Chem. News, nos. 1375-1378, 1886), I proposed for the chemical elements the general formula $A_n B_{2n + (2-x)}$, in which n is the series and x the group to which the element belongs; $A = 12$ and $B = -2$.

Since that time, and for thirteen years previously, I have made frequent attempts to find a simple numerical expression for the Periodic Law, but so far without marked success. Early in the past summer, however, I obtained an expression which, though only approximate, may still be found of considerable interest. According to this

$$A = c(m + v^{\frac{1}{x}}) \quad \text{or} \quad \frac{A}{m + v^{\frac{1}{x}}} = c,$$

in which A = atomic weight, c = constant, m = a member of an arithmetical progression depending on the series* to which the element belongs, v = the maximum valency or the number of the group* of which the element is a member.

After numerous trials it has been found that the best results are obtained when $x = 2$, and

$m = 0; 2\frac{1}{2}; 5; 8\frac{1}{2}; 12; 15\frac{1}{2}; 19; 22\frac{1}{2}; 26; 29\frac{1}{2};$ and 33
for
Series II.; III.; IV.; V.; VI.; VII.; VIII.; IX.; X.; XI.; and XII.
So that

$$\frac{A}{m + \sqrt{v}} = c.$$

It will be observed that m is a member of an arithmetical series in which the common difference is $3\frac{1}{2}$, except in the first two cases, where it is only $2\frac{1}{2}$.

In the following Table are given the values of c calculated from the above equation. The atomic weights employed and given in Column I. are taken from Clarke's 'Recalculation of the Atomic Weights' (1882), corrections being made when rendered necessary by more exact determinations published since Clarke's work. The atomic weights are given to the first place of decimals only.

* These terms are employed in the sense in which Mendeljeff uses them in his Natural Classification of the Elements.

TABLE I.

EVEN SERIES.	I.	II.	ODD SERIES.	I.	II.
	Atomic weight. A.	$\frac{c. (Calc.)}{m + \sqrt{v}}$ A		Atomic weight. A.	$\frac{c. (Calc.)}{m + \sqrt{v}}$ A
SERIES II. $m=0$.	(H=1)		SERIES III. $m=2\frac{1}{2}$.		
Lithium	7.0	7.00	Sodium	23.0	6.57
Beryllium	9.1	6.45	Magnesium	24.4 ¹	6.24
Boron	10.9	6.30	Aluminium	27.0	6.38
Carbon	12.0	6.00	Silicon	28.3 ²	6.29
Nitrogen	14.0	6.25	Phosphorus	31.0	6.54
Oxygen	16.0	6.53	Sulphur	32.0	6.46
Fluorine	18.9	7.13	Chlorine	35.4	6.87
Mean...		6.52	Mean...		6.48
SERIES IV. $m=5$.			SERIES V. $m=8\frac{1}{2}$.		
Potassium	39.0	6.50	Copper	63.3	6.66
Calcium	40.0	6.24	Zinc	65.3	6.59
Scandium	44.0	6.54	Gallium	68.9	6.73
Titanium	48.0	6.86	Germanium	72.3	6.88
Vanadium	51.3	7.09	Arsenic	74.9	6.97
Chromium	52.0	6.98	Selenium	78.8	7.20
Manganese	54.0	7.06	Bromine	79.8	7.16
Mean...		6.75	Mean...		6.88
SERIES VI. $m=12$.			SERIES VII. $m=15\frac{1}{2}$.		
Rubidium	85.3	6.56	Silver	107.7	6.53
Strontium	87.4	6.52	Cadmium	111.8	6.61
Yttrium	89.8	6.54	Indium	113.4	6.58
Zirconium	90.4 ³	6.46	Tin	117.7	6.72
Niobium	94.0 ³	6.60	Antimony	119.6 ⁴	6.74
Molybdenum	95.5	6.61	Tellurium	125.0 ⁵	6.96
Mean...		6.55	Iodine	126.5	6.97
SERIES VIII. $m=19$.			SERIES IX. $m=22\frac{1}{2}$.		
Cæsium	132.6	6.61	Wanting.		
Barium	136.8	6.70			
Lanthanum	138.0 ⁶	6.66			
Cerium	139.9 ⁷	6.66			
Didymium	142.0 ⁶	6.69			
Mean...		6.66			

¹ Marignac (1884).

² Meyer, Mod. Theor. p. 89 (1888).

³ Cleve (1883).

⁴ Thorpe & Young (1887).

⁵ Cooke.

⁶ Brauner (1883).

⁷ Cleve (1883).

Table I. (*continued*).

EVEN SERIES.	I.	II.	ODD SERIES.	I.	II.
	Atomic weight. A.	$\frac{c}{\text{(Calc.) A}}$ $m + \sqrt{v}$		Atomic weight. A.	$\frac{c}{\text{(Calc.) A}}$ $m + \sqrt{v}$
SERIES X. $m=26$. Tantalum Tungsten	(H=1)		SERIES XI. $m=29\frac{1}{2}$. Gold Mercury Thallium Lead Bismuth		
	182.1	6.45		196.9 ⁹	6.46
	183.6	6.45		199.7	6.46
				203.7	6.52
				206.5	6.56
				208.2 ¹⁰	6.56
	Mean...	6.45		Mean...	6.51
SERIES XII. $m=33$. Thorium Uranium	231.9	6.62 ¹¹	General Mean = 6.64.		
	238.5	6.72			
	Mean...	6.67			

⁹ Thorpe & Laurie (1887). ¹⁰ Marignac (1884). ¹¹ Kruss & Nilson (1887).

From the above Table it will be seen that the values of c as calculated from the atomic weights of 55 elements, using the equation referred to, lie between 6.0 and 7.2, with a mean value of 6.64. The lowest value, 6.0, is obtained in the case of carbon, and the highest, 7.2, in that of selenium. In the great majority of cases, however, the value lies much nearer to the mean value than is indicated by the two extremes mentioned, thus:—

In 1 case the value of c lies at 6.0.					
With one exception (Si), all these occur in Groups 1 to 3.	0	"	"	6.1, <i>i. e.</i> between	6.05–6.15
	2	"	"	6.2, "	6.15–6.25
	3	"	"	6.3, "	6.25–6.35
	1	"	"	6.4, "	6.35–6.45
	15	"	"	6.5, "	6.45–6.55
	35	"	"	6.6, "	6.55–6.65
	11	"	"	6.7, "	6.65–6.75
	9	"	"	6.8, "	6.75–6.85
	0	"	"	6.9, "	6.85–6.95
	3	"	"	7.0, "	6.95–7.05
With one exception (Li), all these occur in Groups 4 to 7.	5	"	"	7.1, "	7.05–7.15
	3	"	"	7.2, "	7.15–7.20
	2	"	"		

All the values of c , except that for carbon, lie between 6.24 and 7.20. Of the 55 values of c , 35 lie between 6.45 and 6.75. Of the other 20 values of c , which are farthest from the mean, 11 occur in groups 5, 6, and 7, and of these

10 are higher than the mean, whilst of the 9 remaining values 5 occur in groups 1, 2, and 3, and of these five, four are lower than the mean, so that the high values of c occur chiefly with elements belonging to the higher groups (viz. 5, 6, and 7), while the low values occur chiefly with elements belonging to the lower groups (viz. 1, 2, and 3). Four of the values furthest from the mean occur in group 4; of these two (Ti and Ge) are high, and two (C and Si) are low values of c .

It will be observed that the elements of group 8 have not been included in the above table on account of the difficulty of assigning a value to v in their case. This difficulty, however, is removed if v represents, not the valency, but the *numerical order* of the elements in the series to which they respectively belong, in which case c has the following values in group 8:—

$m=5.$	$m=12.$	$m=19.$	$m=26.$	
Fe...7·14	Ru...6·98	Wanting.	Os...6·69	$v=8.$
Co...7·34	Rh...6·94		Ir ...6·64	$v=9.$
Ni...7·18	Pd...7·00		Pt ..6·66	$v=10.$

For potassium $m=5$, so that the equation $A=6\cdot6(m+\sqrt{v})$ becomes $A=6\cdot6(5+\sqrt{v})$ for the elements of the potassium series; and since the common difference in the arithmetical series 5, $8\frac{1}{2}$, 12, $15\frac{1}{2}$ &c. is $3\frac{1}{2}$, therefore for any element in series IV. or upwards

$$A=6\cdot6[5+3\cdot5(a-4)+\sqrt{v}]=6\cdot6(3\cdot5a-9+\sqrt{v}),$$

where a =the number of the series to which the element belongs, and v the numerical order of the element in its own series.

The equation $A=c(m+\sqrt{v})$ becomes $A=c(m+1)$ in the case of elements belonging to the first group. So that for potassium and silver,

$$(1) \quad c(m_4+1)=39, \quad \text{and} \quad (2) \quad c(m_7+1)=107\cdot7.$$

Let x represent the common difference in the arithmetical series m_4 , m_5 , m_6 , m_7 , &c. corresponding to the 4th, 5th, 6th, 7th, &c. series of elements.

Then

$$m_7=m_4+3x \quad (3).$$

By substituting (3) in (2) we get

$$107.7 = c(m_4 + 3x + 1) = c(m_4 + 1) + 3xc.$$

But

$$c(m_4 + 1) = 39;$$

$$\therefore 107.7 = 39 + 3xc \quad \text{or} \quad xc = 22.90.$$

By proceeding in a similar manner the following values of xc are obtained from the pairs of elements (all belonging to group 1) named:—

From K and Cu . . .	$xc = 24.30$
„ K and Rb . . .	$xc = 23.15$
„ K and Ag . . .	$xc = 22.90$
„ K and Cs . . .	$xc = 23.40$
„ K and Au . . .	$xc = 22.56$
„ Cu and Rb . . .	$xc = 22.00$
„ Cu and Ag . . .	$xc = 22.20$
„ Cu and Cs . . .	$xc = 23.10$
„ Cu and Au . . .	$xc = 22.22$
„ Rb and Ag . . .	$xc = 22.40$
„ Rb and Cs . . .	$xc = 23.65$
„ Rb and Au . . .	$xc = 22.32$
„ Ag and Cs . . .	$xc = 24.90$
„ Ag and Au . . .	$xc = 22.30$
„ Cs and Au . . .	$xc = 21.43$

$$\text{Mean} = 22.85$$

Or, in other words, the difference between the atomic weights of any two elements in group 1 (from series IV. upwards) divided by the difference between the number of the series to which each element belongs, gives a constant, or

$$\frac{B - A}{y - x} = \text{constant} = 22.85,$$

where x and y are the numbers of the series to which the elements A and B respectively belong. That is to say, the difference between successive elements of group 1 from series IV. upwards is practically constant and equal to 22.85.

Now the constant 22.85 is very nearly identical with the atomic weight of sodium, which the most trustworthy determinations have shown to be 22.99.

If x be $3\frac{1}{2}$, then $c = \frac{22.85}{3.5} = 6.53$, or if, in place of 22.85, we take the atomic weight of sodium, then $c = \frac{22.99}{3.5} = 6.57$,

a number which is very nearly identical with 6·64, which was obtained as the value of c by applying the equation $c = \frac{A}{m + \sqrt{v}}$ to all the atomic weights, as in Table I.

If there be any truth in the above, then the atomic weights at present accepted for caesium (132·6) and copper (63·3) are rather too high, and that for gold (196·9) somewhat too low. Caesium should be about 131, copper about 62, and gold about 198.

In Table II. (pp. 104, 105) is given a list of the atomic weights calculated from the equation $A = c(m + \sqrt{v})$, c being taken equal to 6·6.

The Table shows that, of the 54 elements considered, the difference between the calculated and experimental atomic weights

33	{	in the case of 21 elements is less than	1 unit	
	{	" " 12 " it lies between 1 & 1½ units	2 & 3	"
	{	" " 8 " " "	3 & 3½	"
21	{	" " 3 " " "	4 & 4½	"
	{	" " 6 " " "	6 & 6¾	"
	{	" " 4 " " "		
				Mean ± 1·9

The considerable difference between the calculated and experimental values in some cases shows that the expression At. wt. = 6·6 ($m + \sqrt{v}$) is at best only approximate. The atomic weights calculated by it are, however, very much nearer the experimental values than those calculated according to Dulong and Petit's law from the equation

$$\text{At. wt.} = \frac{\text{atomic heat}}{\text{specific heat}} = \frac{6\cdot4}{\text{spec. ht.}}$$

Thus of the 44 elements* of which the specific heats have been directly determined, the difference between the calculated and experimental atomic weights

14	{	in the case of 9 elements is less than	1 unit	
	{	" " 5 " it lies between 1 & 1½ units	1½ & 2	"
	{	" " 2 " " "	2 & 3	"
	{	" " 5 " " "	3 & 4	"
23	{	" " 4 " " "	4 & 5	"
	{	" " 2 " " "	5 & 6	"
	{	" " 5 " " "	6 & 7	"
	{	" " 2 " " "	7 & 10	"
7	{	" " 5 " " "	10 & 15	"
				Mean ± 4·2

* Exclusive of C, Si, B, N, O, F, and H, which are apparently such marked exceptions to Dulong and Petit's law.

TABLE II.

EVEN SERIES.	I.		II.		III.	Dif- ference.	Spec. grav.	Spec. vol.	
	Atomic weight.							Expt. I. III.	Calc. II. III.
	Expt. See Table I.	Calculated $6\cdot6(m+\sqrt{v})$.							
SERIES II. $m=0$.	ODD SERIES.								
	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								
	Aluminium								
	Silicon								
	Phosphorus								
	Sulphur.....								
SERIES IV. $m=5$.	SERIES V. $m=8\frac{1}{2}$.								
	Copper								
	Zinc								
	Gallium.....								
	Germanium								
	Arsenic								
	Selenium								
SERIES II. $m=0$.	SERIES III. $m=2\frac{1}{2}$.								
	Sodium								
	Magnesium								

SERIES VI. $m=12$. Rubidium Strontium Yttrium Zirconium Niobium Molybdenum ...	85.3	85.8	+0.5	1.52	56.1	56.4	SERIES VII. $m=15\frac{1}{2}$. Silver Cadmium Indium Tin Antimony Tellurium Iodine	107.7	108.9	+1.2	10.5	10.2	10.4
	87.4	88.5	+1.1	2.50	34.9	35.4		111.8	111.6	-0.2	8.65	12.9	12.9
	89.8	90.6	+0.8	?	?	?		113.4	113.7	+0.3	7.42	15.3	15.3
	90.4	92.4	+2.0	4.15	21.7	22.3		117.7	115.5	-2.2	7.29	16.1	15.8
	94.0	94.0	0	6.27	15.0	15.0		119.6	117.1	-2.5	6.7	17.9	17.5
	95.5	95.4	-0.1	8.6	11.1	11.1		125.0	118.5	-6.5	6.25	20.0	19.0
								126.5	119.8	-6.7	4.94	25.6	24.2
SERIES VIII. $m=19$. Cesium Barium Lanthanum Cerium	132.6	132.0	-0.6	1.88	70.6	70.2	SERIES IX. $m=22\frac{1}{2}$. Wanting.						
	136.8	134.7	-2.1	3.75	36.5	35.9							
	138.0	136.8	-1.2	6.2	22.2	22.1							
	139.9	138.6	-1.3	6.7	20.9	20.7							
SERIES X. $m=26$. Tantalum Tungsten	182.1	186.4	+4.3	10.8	16.9	17.2	SERIES XI. $m=29\frac{1}{2}$. Gold Mercury Thallium Lead Bismuth	196.9	201.3	+4.4	19.3	10.2	10.1
	183.6	187.8	+4.2	19.13	9.6	9.8		199.7	204.0	+4.3	13.59	14.7	15.0
								203.7	206.1	+2.4	11.86	17.2	17.4
								206.5	207.9	+1.4	11.38	18.1	18.3
								208.2	209.5	+1.3	9.82	21.2	21.3
SERIES XII. $m=33$. Thorium Uranium	231.9	231.0	-0.9	11.1	20.9	20.8							
	238.5	234.0	-4.5	18.7	12.7	12.5							

In Table II. is given not only the atomic weights as accepted by the best authorities and as calculated by the formula $A = 6.6(m + \sqrt{v})$, but also the specific gravities*, together with the specific volumes as calculated both from the experimental and from the calculated atomic weights, by dividing each of these respectively by the corresponding specific gravities. From the Table it will be seen that the specific volumes as found by each of these two processes agree closely. Further, if two curves be constructed in the manner first suggested by Lothar Meyer, by taking in the one case the experimental atomic weights as abscissæ, and the corresponding specific volumes as ordinates, and in the other case the atomic weights calculated from $A = 6.6(m + \sqrt{v})$ as abscissæ and the corresponding specific volumes as ordinates, then the result represented in Diagram I. will be obtained, in which the dotted curve, being constructed from the experimental atomic weights†, may be called the experimental curve; while the continuous one, being constructed by using the calculated atomic weights, may be called the calculated curve.

It will be seen from both Table II. and from Diagram I. that the greatest differences between the calculated and experimental atomic weights occur chiefly at the end of series IV., V., and VII., and at the beginning of series XI.

It has been shown that in the equation $A = c(m + \sqrt{v})$ the constant c has a mean value of 6.6. Supposing that there is any truth in the equation, what is the meaning of the constant 6.6? This number at once suggests the constant 6.4, obtained according to Dulong and Petit's law, by multiplying the atomic weight by the specific heat. If in the equation $A = c(m + \sqrt{v})$ we assume that the constant c represents the atomic heat, then,

$$\begin{aligned}\text{Atomic weight} &= \text{atomic heat} \times (m + \sqrt{v}) \\ &= \text{atomic weight} \times \text{specific heat} \times (m + \sqrt{v}); \\ \therefore \quad 1 &= \text{specific heat} \times (m + \sqrt{v}), \\ \text{or specific heat} &= \frac{1}{m + \sqrt{v}}.\end{aligned}$$

If the specific heats of the several elements be calculated by this equation, we find that in almost all cases the calculated numbers agree very closely with the experimental specific heats. This will be seen from the following Table:—

* Taken from Lothar Meyer's *Mod. Theories*, p. 123; translated by Bedson and Williams.

† It is identical with Lothar Meyer's curve.

TABLE III.

	Specific Heat calculated from $\frac{1}{m + \sqrt{v}}$	Specific Heat (experiment).		
		Specific Heat.	Temp. of determination *.	Authority.
SERIES II. $m=0$.				
Lithium	1.000	.941	C. 64°	Regnault.
Beryllium709	.642	100	Reynolds.
Boron578	.582	257	Nilson and Peterson.
Carbon { graphite } { diamond }	.500	.5 (?)	600	Weber.
Nitrogen446	.467	978	"
Oxygen408	.459	985	"
Fluorine377	[.36]†		
		[.25]†		
		[.26]†		
SERIES III. $m=2\frac{1}{2}$.				
Sodium286	.293	-14	Regnault.
Magnesium255	.250	60	"
Aluminium236	.214	60	"
		.225	...	Mallet.
		.216	50	Naccari.
		.240	300	"
Silicon222	.203	232	Weber.
Phosphorus (yellow)	.211	.189	20	Regnault.
		.202	25	Kopp.
		.212	75	Person.
		.178	67	Regnault.
		.188	...	Dulong and Petit.
Sulphur (rhombic)...	.202	.202	...	Regnault.
		.209	...	Neumann.
		.235	134	Person.
Chlorine194	.180†		
SERIES IV. $m=5$.				
Potassium164	.166	-34	Regnault.
Calcium156	.170	50	Bunsen.
Scandium.....	.148	.145†		
		.112	50	Nilson and Peterson.
Titanium143	.162	220	"
Vanadium138	.124†		"
Chromium134	.122†		"
Manganese (two samples)131	.122		
		.133	55	Regnault.

* These temperatures are the arithmetical mean of the extreme temperatures between which the specific heats were determined.

† Not determined directly, but by calculation from the experimental specific heats of the compounds.

‡ Calculated from Dulong and Petit's law. $\text{Sp. ht.} = \frac{6.4}{\text{at. wt.}}$.

Table III. (continued).

	Specific Heat calculated from $\frac{1}{m + \sqrt{c}}$.	Specific Heat (experiment).		
		Specific Heat.	Temp. of determination*.	Authority.
SERIES V. $m=8\frac{1}{2}$.				
Copper.....	.105	.093	C. 35	Kopp.
		.095	58	Regnault.
		.093	50	Naccari.
		.099	300	"
		.095	50	Dulong and Petit.
Zinc101	.101	150	"
		.093	33	Kopp.
		.094	50	Bunsen.
		.096	55	Regnault.
		.094	50	Dulong and Petit.
Gallium097	.102	150	"
		.093	50	Naccari.
		.104	300	"
Germanium095	.079	18	Berthelot.
Arsenic (crystalline)	.093	.076	270	Nilson and Peterson.
		.081	55	Regnault.
		.082	56	Neumann.
		.091	13	Regnault.
Selenium $\left\{ \begin{array}{l} \text{(crystal-} \\ \text{line)} \\ \text{(crystal-} \\ \text{line)} \\ \text{(amor-} \\ \text{phous)} \end{array} \right\}$.091	.076	59	"
		.086	61	Neumann.
Bromine (solid)089	.095	?	Bettendorf and Willner.
		.084	-51	Regnault.
SERIES VI. $m=12$.				
Rubidium077	.077†		
Strontium074	.074†		
Yttrium073	.072†		
Zirconium071	.067	50	Mixter and Dana.
Niobium070	.068†		
Molybdenum069	.066	10	Delarive and Marcet.
		.072	55	Regnault.

* These temperatures are the arithmetical mean of the extreme temperatures between which the specific heats were determined.

† Not determined directly, but by calculation from the experimental specific heats of the compounds.

‡ Calculated from Dulong and Petit's law. $\text{Sp. ht.} = \frac{6.4}{\text{at. wt.}}$.

Table III. (continued).

	Specific Heat calculated from $\frac{1}{m + \sqrt{v}}$.	Specific Heat (experiment).		
		Specific Heat.	Temp. of determination*.	Authority.
SERIES VII. $m=15\frac{1}{2}$.				
Silver	·061	·056	O. 50; 36	Bunsen; Kopp.
		·057	55	Regnault.
		·056	50	Dulong and Petit.
		·061	150	"
		·057	25	Byström.
		·061	150	"
		·056	50	Naccari.
		·061	300	"
		·063	?	Potter.
		·054	37	Kopp.
Cadmium.....	·059	·055	50	Bunsen.
		·058	10	Delarive and Marcet.
		·059	13	Regnault.
		·055	50	Naccari.
Indium.....	·058	·062	300	"
		·057	50	Bunsen.
		·055	34	Kopp.
Tin	·057	·056	50	Bunsen.
		·056	55	Regnault.
		·055	58	Bede.
		·058	115	"
		·050	50	Bunsen.
Antimony	·056	·051	55	Regnault.
		·052	31	Kopp.
		·049	50	Naccari.
		·054	300	"
		·051	50	Dulong and Petit.
		·055	150	"
		·050	17	Pebal and Jahn.
		·056	17	"
(ordinary form)		·047+	36	Kopp.
(explosive form)		·047+	55	Regnault.
Tellurium (distilled)	·055	·052+	55	"
(undistilled)		·054	59	"
Iodine	·055			
SERIES VIII. $m=19$.				
Cæsium	·050	·048+		
Barium	·049	·047+		
Lanthanum	·048	·045	50	Hildebrand.
Cerium.....	·048	·045	49	"
		·05		Schuchardt.
Didymium	·047	·046		Hildebrand.

* These temperatures are the arithmetical mean of the extreme temperatures between which the specific heats were determined.

† It is very doubtful whether the Tellurium employed was pure. Compare Brauner, Chem. Soc. Journ. lv. p. 382.

‡ Calculated from Dulong and Petit's law. $\text{Sp. ht.} = \frac{6.4}{\text{at. wt.}}$

Table III. (*continued*).

	Specific Heat calculated from $\frac{1}{m + \sqrt{v}}$.	Specific Heat (experiment).		
		Specific Heat.	Temp. of determination*.	Authority.
SERIES IX. $m = 22\frac{1}{2}$.	wanting.			
SERIES X. $m = 26$.				
Tantalum.....	·035	·035†	55	Regnault. Delarive and Marcet. Regnault.
Tungsten	·0351	·0334	11	
		·035		
		·0364		
SERIES XI. $m = 29\frac{1}{2}$.				
Gold.....	·0328	·0329	55	Regnault.
Mercury (solid)	·0323	·0319	—59	"
Thallium	·0320	·0325		Lamy.
		·0335	58	Regnault.
		·0314	55	"
		·0315	34	Kopp.
Lead.....	·0317	·0305	61	Bede.
		·0317	94	"
		·0304	50	Naccari.
		·0338	300	"
Bismuth	·0315	·0305	34	Kopp.
		·0308	55	Regnault.
		·0309	?	Schmidaritsch.
SERIES XII. $m = 33$.				
Thorium	·0285	·0276	50	Nilson.
Uranium	·0282	·0277	49	Zimmerman.

* These temperatures are the arithmetical mean of the extreme temperatures between which the specific heats were determined.

† Calculated from Dulong and Petit's law. Sp. ht. = $\frac{6.4}{\text{at. wt.}}$.

The specific heats of nitrogen, oxygen, and fluorine have not been determined in the solid state, while the values obtained from the specific heats of their compounds are well known to be abnormally low, as are those of beryllium, boron, carbon, and silicon, which have been determined directly with the elements in the solid state. Even in the case of the latter elements, the values calculated from the expression $\frac{1}{m + \sqrt{v}}$ are not very far from the experimental numbers, while in all others, except those of calcium, gallium, and germanium, the agreement is remarkably close. The experimental value for calcium is apparently too high, being greater than that of potas-

sium, whereas, according to Dulong and Petit's law, it should be less. The experimental values for gallium and germanium, on the other hand, are, according to Dulong and Petit's law, apparently much too low, being less even than that of bromine, although this element has an atomic weight about 10 units higher. The atomic heat of gallium is only 5.4, and that of germanium only 5.5; whereas the specific heats calculated from the expression $\frac{1}{m + \sqrt{v}}$ would give rather less than 6.7 and 6.9 respectively.

It may be said that of the 55 elements with which the comparison can be made, the calculated specific heats agree very closely with the experimental values in the case of 45 of them, while the other ten are elements the specific heats of which, according to Dulong and Petit's law, are more or less abnormal.

The agreement becomes even more marked when the comparison is made with specific heats determined at temperatures above those at which specific heats have been more commonly determined.

Diagram II. shows graphically the close agreement between the calculated and experimental specific heats. It is constructed by taking the atomic weights as abscissæ and the specific heats as ordinates. The dotted curve is constructed from the calculated and the continuous one from the experimental specific heats. The specific heats used in the latter case are chiefly those given on page 89 of Lothar Meyer's 'Modern Theories,' translated by Williams and Bedson. If, however, those determinations which agree more nearly with the calculated numbers were used, the two curves would coincide even more closely.

In the equation $A = c(m + \sqrt{v})$ the constant c is equal to 6.6, and has been assumed to represent the atomic heat of the elements, whereas the atomic heat, on the basis of Dulong and Petit's law, is usually taken to be 6.4. This latter value, however, is obtained because the specific heats employed are mostly those which have been determined between 0° and 100° C., whereas if the specific heats obtained at higher temperatures (say 0° to 300°) be employed a somewhat higher value, approximating to 6.6, will be found for the atomic heat.

As is well known, the specific heat, and therefore the atomic heat likewise, increases, though very slowly, with the temperature. If c , therefore, really represents the atomic heat, it is not strictly but only approximately a constant, being a function of the temperature. Consequently, in each of the

equations

$$A = c \times \text{spec. heat (Dulong and Petit's law).}$$

$$A = c(m + \sqrt{v}),$$

the atomic weight A is not exactly but only approximately equal to the expressions on the right-hand side, since the latter are a function of the temperature, whereas the atomic weight, so far as we know, is constant.

According to Bettone the hardness of an element is inversely proportional to its specific volume. If this be so, then hardness may be represented in terms of the specific gravity and the expression $6.6(m + \sqrt{v})$, thus

$$\text{Hardness} = \frac{1}{\text{spec. vol.}} = \frac{\text{sp. gr.}}{\text{at. wt.}} = \frac{\text{sp. gr.}}{6.6(m + \sqrt{v})}.$$

The following Table gives the hardness of a number of elements as found experimentally by Bettone, and as calculated by the above equation:—

	Specific gravity.	Hardness.	
		Calculated.	Found (Bettone).
		$\frac{\text{sp. gr.}}{6.6(m + \sqrt{v})}$	
Carbon (diamond) ...	3.3	.250	.301
Manganese	8.0	.158	.146
Copper	8.8	.140	.136
Zinc	7.15	.109	.108
Silver.....	10.5	.0964	.099
Gold	19.3	.096	.098
Aluminium	2.56	.092	.082
Cadmium	8.65	.077	.076
Magnesium	1.74	.071	.073
Tin.....	7.29	.063	.065
Lead	11.38	.055	.057
Thallium	11.86	.057	.056
Calcium... ..	1.57	.037	.041
Sodium97	.042	.040
Potassium.....	.86	.022	.023

It should be noted, however, that Bettone's values, on which he founds his law of hardness, do not agree in several cases with those found by other observers, *i. e.* Calvert and Johnson.

In the expression $A = c(m + \sqrt{v})$ it has been stated that m is the member of an arithmetical progression. For even

series m is a whole number, whereas in the odd series it is a whole number and a half, thus corresponding to the well-known difference between elements of even series on the one hand and odd series on the other.

Again, in the arithmetical series,

$$0; 2\frac{1}{2}; 5; 8\frac{1}{2}; 12; 15\frac{1}{2}; 19; 22\frac{1}{2}; 26; 29\frac{1}{2}; 33$$

the common difference in the case of the first three members is only $2\frac{1}{2}$, whereas after that point it is $3\frac{1}{2}$; this corresponds to the statement of Mendeljeff that the 2nd and 3rd series (*i. e.* Li and Na series) of elements are more or less exceptional in their character and not strictly comparable with the subsequent series.

IX. *On two Pulsating Spheres in a Liquid.*

By A. L. SELBY, M.A., *Fellow of Merton College, Oxford* *.

A SPHERE is said to pulsate when it periodically dilates and contracts.

If two pulsating spheres are immersed in a liquid, inequalities of pressure in the liquid arise, and there is generally a resultant pressure on each sphere urging it towards or away from the other.

An approximate expression of this is given in Basset's 'Hydrodynamics' (vol. i. p. 255), but the proof is rather long, involving an integration of pressures over the surface of a sphere.

By a somewhat different method I have obtained in § 5 an expression which may be carried further than Mr. Basset's without much labour; and in § 6 I have applied the method to solve the more general problem relating to the case when the radial velocities on the surfaces of the spheres are Zonal Harmonics of the m th and n th degrees respectively, with the line of centres as their axis.

A still more general solution can be derived from this; for when the radial velocities on the spheres are any functions of the distance from the line of centres, each can be expressed as a series of Zonal Harmonics.

Since I wrote this paper I have found one by Prof. Pearson (Trans. Camb. Phil. Soc. vol. xiv. part ii.) in which this problem is investigated; but numerical values of the constants involved are only given for Harmonics of low degree.

In dealing with these questions some propositions on

* Communicated by the Author.

Images, due to Mr. Hicks, are required. His proofs will be found in the 'Philosophical Transactions' for 1880; but in §§ 2-4 of this paper I give other proofs, in which the subject is considered from a slightly different point of view.

The main interest of the problem of pulsating spheres is derived from its experimental illustration by Prof. Bjerknes.

§ 1. *Preliminary Definitions.*—A source of liquid of strength m is a point at which a volume of liquid $4\pi m$ is supplied per unit time. A sink (or negative source) of equal strength is a point at which liquid disappears at the same rate. A combination of a source and sink of equal numerical strength m , at an infinitesimal distance d apart, is a doublet. As this is analogous to an infinitely small magnet, I shall call md the moment of the doublet. The intensity of a doublet is its moment divided by its length; it is analogous to the intensity of magnetization of a bar of unit section. The axis of a doublet is the line from the sink to the source.

The lines of flow due to any distribution of sources and sinks are the lines of force due to the corresponding magnetic poles.

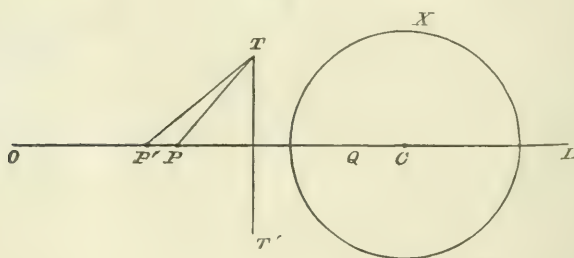
§ 2. Let P, P' be a source m and sink $-m$ on the straight line OL :

$$TPL = \theta; \quad TP'L = \theta'; \quad TP = r; \quad PP' = d.$$

Then the flow through the circle (of which TT' is the projection) formed by revolving T round OL is

$$2\pi m (\cos \theta' - \cos \theta).$$

Fig. 1.



Let P' approach P so that PP' diminishes indefinitely, md retaining a constant magnitude μ . Then

$$2\pi m (\cos \theta' - \cos \theta) = 2\pi \mu \sin^2 \theta \cdot /r.$$

If the source and sink are interchanged, the sign of the flow is reversed; we may consider μ as negative in this case.

Let a doublet of moment $-\mu'$ be placed at Q, where $\mu > \mu'$. If $TQL = \phi$, $TQ = r'$, the flow through TT' due to this is

$$-2\pi\mu' \sin^2 \phi \cdot /r'.$$

The equation of a surface of revolution across which there is no flow from the doublets at P and Q is

$$2\pi(\mu \sin^2 \theta \cdot /r - \mu' \sin^2 \phi \cdot /r) = A, \text{ a constant.}$$

If $A=0$, this reduces to the line OL and the sphere $\mu r^{-3} = \mu' r'^{-3}$.

If C be the centre of this sphere and a the radius,

$$CP \cdot CQ = a^2 \quad \text{and} \quad a = (x^2 - 1)PQ/2x,$$

where $\alpha^3 = \mu/\mu'$.

Since the liquid is supposed to be "perfect," and the sphere is part of a surface of flow, we may make a material sphere occupy its place.

Hence the effect of a sphere X (fig. 1) in disturbing the flow from the doublet μ at P, distant f from its centre, is the same as if the sphere were removed and a doublet $-\mu\alpha^3/f^3$ placed at Q. This doublet is called the image of μ in the sphere.

§ 3. To determine the image of a source μ at P.

This source is equivalent to a line of doublets of intensity μ extending from P to infinity along PO (fig. 1). Its image is therefore a line of doublets from Q to C.

If μd be the moment of a doublet distant a^2/x from the centre, $-\mu d x^3/a^3$ is the moment of its image. But the lengths of corresponding parts of $P\infty$ and CQ are as $a^2 : x^2$.

Therefore the intensity of the image is $-\frac{\mu x}{a}$, supposing the axis along QC ; or $\frac{\mu x}{a}$, regarding it as along CQ .

Now a magnet of length l and unit section, whose intensity of magnetization at a distance x from one end is Cx , is equivalent (so far as concerns external action) to a quantity of "magnetic matter" C at the positive end, and a distribution of line-density $-C$ along the axis.

Therefore, from the analogy between sources and magnetic poles, the line of doublets is equivalent to a source $\mu a/f$ at Q, and a line sink of strength $-\mu/a$ per unit length along CQ .

§ 4. To find the image of a system of doublets PQ (fig. 2) of intensity μx , where x is the distance from Q.

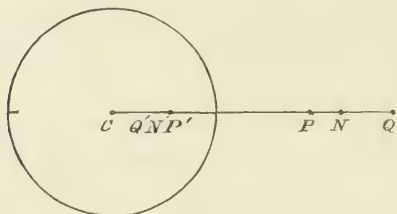
Let P' , Q' be the points inverse to P and Q.

By § 2 the image is a system of doublets lying between P' and Q' .

Let N be a point on PQ , N' its image, $QN = x$, $CP = f$.

By § 3 the image of a doublet of intensity μx at N is of intensity $-\mu x CN'/a$ or $-\mu CQ \cdot Q'N'/a$.

Fig. 2.



The image of the system PQ is therefore a line of doublets in which the intensity is proportional to the distance from Q' , and the image is similar to the system from which it is derived.

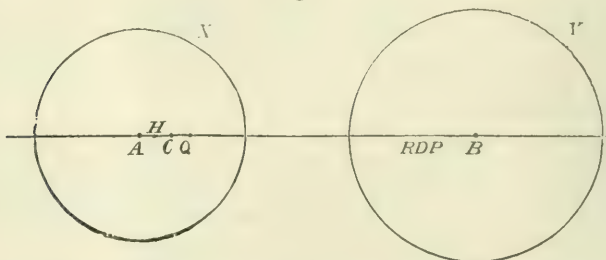
This result is easily transformed by the process used in § 3 into the following:—

The image of a source μ at P and a line-sink PQ of strength $-\frac{\mu}{PQ}$ per unit length is a source $\mu \cdot a/f$ at P' and a line-sink $P'Q'$ of strength $-\frac{\mu a}{f \cdot P'Q'}$.

It is clear that any system of sources and sinks of total strength zero distributed along PQ has for its image another such system distributed along $P'Q'$. For the given system can be reduced to a system of doublets.

§ 5. To determine the stress between two spheres X , Y , pulsating in an infinite liquid.

Fig. 3.



Let A , B be the centres of the spheres (fig. 3); a , b the radii. Then \dot{a} , \dot{b} are the normal velocities at the surfaces.

Let ϕ_A be the velocity-potential in the liquid when A pulsates and B does not, ϕ_B the velocity-potential when B pulsates and A does not. Then $\phi_A + \phi_B$ is the velocity-potential when both pulsate.

For if n_1, n_2 are normals to X, Y, drawn into the liquid,

$$d\phi_A/dn_1 = \dot{a}, \quad d\phi_B/dn_2 = \dot{b}, \quad d\phi_A/dn_2 = 0, \quad d\phi_B/dn_1 = 0. \quad (1)$$

Therefore, if $\phi_A + \phi_B = \phi$,

$$d\phi/dn_1 = \dot{a} \quad \text{and} \quad d\phi/dn_2 = \dot{b}.$$

Also ϕ satisfies Laplace's equation, and vanishes at infinity.

If T be the kinetic energy of the liquid, ρ its density,

$$\begin{aligned} \frac{2T}{\rho} &= \iiint \left\{ \left(\frac{d\phi}{dx} \right)^2 + \left(\frac{d\phi}{dy} \right)^2 + \left(\frac{d\phi}{dz} \right)^2 \right\} dx dy dz \\ &= - \iint \phi \frac{d\phi}{dn_1} dS_1 - \iint \phi \frac{d\phi}{dn_2} dS_2, \quad . \quad . \quad . \quad (2) \end{aligned}$$

the volume-integration extending through the liquid, and the surface-integrals being taken over S_1, S_2 , the surfaces of X and Y.

But by the surface conditions (1) and by Green's theorem,

$$\iint \phi_B \frac{d\phi}{dn_1} dS_1 = \iint \phi_A \frac{d\phi}{dn_2} dS_2. \quad . \quad . \quad . \quad (3)$$

Substituting $\phi_A + \phi_B$ for ϕ in (2), and employing (1) and (3), we have

$$2T/\rho = -\dot{a} \iint \phi_A dS_1 - 2\dot{b} \iint \phi_A dS_2 - \dot{b} \iint \phi_B dS_2. \quad (4)$$

Let P (fig. 3) be the inverse of A in the sphere Y; Q, C the inverses of P, B in X; R, D the inverses of Q, C in Y.

If Y were absent, the pulsations of X would give the same velocity-potential as a source $a^2\dot{a}$ at A.

The image of this in Y is a line of doublets BP; that of BP in X is a line of doublets QC; that of QC in Y is a line of doublets RD; and so on.

Now the flow across the surface X due to BP, QC; RD, ... taken in successive pairs is zero; and the flow across Y due to A, BP; QC, RD; ... taken in pairs is also zero.

ϕ_A is therefore the velocity-potential due to these systems.

It is simpler to transform each line of doublets into the equivalent source and line-sink.

Let $AB=c$, and denote $a^2\dot{a}$ by μ .

The doublets BP reduce to a source $\mu b/c$ at P and a line-sink $-\frac{\mu b}{c \cdot BP}$ along BP.

The doublets QC reduce to a source $\mu ab/(c^2 - b^2)$ at Q and a line-sink $-\frac{\mu ab}{QC(c^2 - b^2)}$ along QC.

We shall find that the doublets RD contribute a term of order c^{-10} to T; this we shall neglect.

The lengths of successive line-sinks diminish very rapidly, each being to its predecessor in a ratio of the order a^2/c^2 or b^2/c^2 .

Therefore, since $BP = b^2/c$, the lengths QC, RD, ... are of order c^{-3}, c^{-5}, \dots , and the strengths of successive sources A, P, Q, ... are of order $1, c^{-1}, c^{-2}, \dots$

If a source ν at distance r from A contribute a term ϕ_ν to ϕ_A , it has been proved by Gauss that

$$\iint \phi_\nu dS_1 = -4\pi a^2 \nu / r \text{ or } -4\pi a \nu, \text{ according as } r > \text{ or } < a. \quad (5)$$

[This may be proved in the following elementary way:—

Let the sphere be an attracting shell of surface-density unity.

$\iint \phi_\nu dS$ is the work done by a particle ν if the sphere recedes to infinity.

And $-4\pi a^2 \nu / r$ or $-4\pi a \nu$ is the work done by the sphere when the particle recedes to infinity, according as $r > \text{ or } < a$.]

Excepting the source μ at A, all the images within A are of total strength zero.

An image outside A consists of a source of strength s distant ρ from A, and a line-sink $-s/\gamma$ per unit-length, with extremities distant $\rho, \rho + \gamma$ from A.

This contributes to the coefficient of $4\pi a^2$ in $-\iint \phi_A dS_1$ the term

$$\frac{s}{\rho} - \int_0^\gamma \frac{s}{\gamma} \frac{dx}{\rho + x},$$

or

$$\frac{s}{\rho} - \frac{s}{\gamma} \log_e \left(1 + \frac{\gamma}{\rho} \right), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is, approximately,

$$s\gamma/2\rho^2 - s\gamma^2/3\rho^3. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For the image PB,

$$s = \mu b/c; \quad \gamma = b^2/c; \quad \rho = c - b^2/c. \quad . \quad . \quad . \quad (8)$$

Therefore this contributes

$$\frac{\mu b}{c^2 - b^2} - \frac{\mu}{b} \log \frac{c^2}{c^2 - b^2}.$$

The source at R is of order c^{-3} ; RD is of order c^{-5} ; AR is of order c .

Therefore RD contributes a term of order c^{-10} .

Omitting terms of this order,

$$- \dot{a} \iint \phi_A dS_1 = 4\pi a^4 \dot{a}^2 \left\{ \frac{1}{a} + \frac{b}{c^2 - b^2} - \frac{1}{b} \log \frac{c^2}{c^2 - b^2} \right\};$$

$- \dot{b} \iint \phi_B dS_2$ can be written down by interchanging a and b .

It remains to form the term $-\dot{\int} \phi_A dS_2$ in (4).

A contributes $a^2 \dot{a}/c$ to the coefficient of $4\pi b^2$; BP contributes nothing.

For QC, $s = \mu ab/(c^2 - b^2)$; $\rho = c - a^2 c/(c^2 - b^2)$, ρ being here reckoned from B;

$$\gamma = \frac{a^2 b^2}{c(c^2 - b^2)}. \quad \dots \dots \dots (9)$$

$s\gamma^2/3\rho^3$ is of order c^{-11} ;

$$\frac{s\gamma}{2\rho^2} = \frac{\mu a^3 b^3}{c^7} \left(\frac{1}{2} + \frac{a^2 + b^2}{c^2} \right);$$

RD contributes nothing, and further images are negligible.

Therefore, to terms of order c^{-9} inclusive,

$$\begin{aligned} \frac{2T}{\rho} = & 4\pi a^4 \dot{a}^2 \left\{ \frac{1}{a} + \frac{b}{c^2 - b^2} - \frac{1}{b} \log \frac{c^2}{c^2 - b^2} \right\} \\ & + 4\pi b^4 \dot{b}^2 \left\{ \frac{1}{b} + \frac{a}{c^2 - a^2} - \frac{1}{a} \log \frac{c^2}{c^2 - a^2} \right\} \\ & + 8\pi a^2 b^2 \dot{a} \dot{b} \left\{ \frac{1}{c} + \frac{a^3 b^3}{2c^7} + \frac{a^3 b (a^2 + b^2)}{c^9} \right\}. \end{aligned}$$

Now the force tending to increase c , required to maintain c at its given value, is $-\frac{dT}{dc}$.

Therefore, if the spheres are free to move they behave as if a force $\frac{dT}{dc}$ tended to separate them, and (omitting for brevity terms beyond c^{-8}),

$$\frac{1}{\rho} \frac{dT}{dc} = - \frac{4\pi a^2 b^2 \dot{a} \dot{b}}{c^2} \left(1 - \frac{7a^2 b^2}{2c^6} \right) - \frac{4\pi a^4 \dot{a}^2 b^3}{c^5} \left(1 + \frac{2b^2}{c^2} \right) - \frac{4\pi b^4 \dot{b}^2 a^3}{c^5} \left(1 + \frac{2a^2}{c^2} \right).$$

If \bar{a} , \bar{b} be the mean radii of the spheres, T the period of vibration, α , β the amplitude of vibration,

$$a = \bar{a} + \alpha \sin \frac{2\pi t}{T}, \quad b = \bar{b} + \beta \sin 2\pi \left(\frac{t}{T} + \epsilon \right);$$

and, supposing the pulsations small, the mean value of the force is (after replacing \bar{a} , \bar{b} by a , b)

$$-\frac{8\pi^3 a^2 b^2}{\rho T^2} \left\{ \frac{\alpha\beta}{c^2} \left(1 - \frac{7a^3 b^3}{2c^6} \right) \cos \frac{2\pi\epsilon}{T} + \frac{ab}{c^5} (a\alpha^2 + b\beta^2) + \frac{2a^2 b^2}{c^7} (b\alpha^2 + a\beta^2) \right\}.$$

If the spheres are not very near, terms after that involving c^{-2} can be neglected, and c tends to diminish or increase according as $\cos \frac{2\pi\epsilon}{T}$ is positive or negative—*i. e.* according as the phases of vibration of the spheres approach more nearly to coincidence or opposition.

§ 6. The above method is also applicable when the displacement on each sphere is a Zonal Harmonic with the line of centres as axis.

Definition.—If $(f, 0, 0)(x, y, z)$ be the coordinates of two points C and P, at a distance r apart, a source at C which gives a potential $-\mu \frac{d^n}{df^n} \left(\frac{1}{r} \right)$ at P is called a source of the n th order.

A doublet is a source of the first order, and a source of the second order is derived from it in the same way as a doublet from a source of order zero (hitherto called a source). A source of the n th order is derived similarly from a source of the $n-1$ th order.

Let H (fig. 3) be the position of a doublet μ distant f from B along BA; and let V be the potential at (x, y, z) due to H and its successive images in Y and X.

Take a doublet μ at H' such that $BH' = f + df$, and a doublet $-\mu$ at H.

The potential at (x, y, z) due to H' and its images is $V + \frac{dV}{df} df$.

Therefore the potential due to a source μ of the second order and its images is $\frac{dV}{df}$, and that due to a source μ of the n th order and its images is $\frac{d^{n-1}V}{df^{n-1}}$.

When the axes of the doublet and of the derived sources are directed towards B, this becomes $(-)^{n-1} \frac{d^{n-1} V}{df^{n-1}}$.

Now let the spheres X, Y vibrate so that the normal velocities are Zonal Harmonics uP_n , vP_m , having AB, BA as their respective axes.

Then, since

$$\mu \frac{d^n}{df^n} \left(\frac{1}{r} \right) = \frac{\mu n! P_n}{r^{n+1}},$$

X, if it vibrated by itself, would behave like a source of the n th order of strength $\frac{a^{n+2} u}{n+1!}$, with its axis along AB.

Let ϕ_A be the potential due to this source and its images. This is found by calculating successive images of the complex source H in Y and X, and making $f=c$ after all operations are completed.

If Y vibrated by itself it would be equivalent to a source of the m th order, $\frac{b^{m+2} v}{m+1!}$; and with its images it would give a potential ϕ_B .

Then, as before, if both spheres vibrate,

$$2T/\rho = -u \iint \phi_A P_n dS_1 - 2v \iint \phi_A P_m dS_2 - v \iint \phi_B P_m dS_2. \quad (10)$$

To evaluate $\iint \phi_A P_m dS_2$, we proceed as follows:—

$$\phi_A = (-)^{n-1} \frac{d^{n-1} \psi}{df_c^{n-1}},$$

where ψ is the potential due to a doublet $\frac{a^{n+2} u}{n+1!}$ (with axis along AB) distant f from B, and to the images of the doublet; the subscript c denoting that after all operations are completed c is to be written for f .

$$\therefore \iint \phi_A P_m dS_2 = (-)^{n-1} \frac{d^{n-1}}{df_c^{n-1}} \iint \psi P_m dS_2.$$

Now, if v be a source of order zero distant ξ from B, ϕ_v its velocity-potential,

$$\iint P_m \phi_v dS_2 = -\frac{4\pi b^{m+2} v}{(2m+1)\xi^{m+1}} \quad \text{or} \quad -\frac{4\pi \xi^m v}{(2m+1)b^{m-1}},$$

according as $\xi >$ or $< b$.

Whence, for a doublet ν at the same point, with axis along AB,

$$\iint P_m \psi_\nu dS_2 = -\frac{4\pi b^{m+2} \nu (m+1)}{(2m+1) \xi^{m+2}} \quad \text{or} \quad \frac{4\pi m \xi^{m-1} \nu}{(2m+1) b^{m-1}},$$

ψ_ν being the velocity-potential due to ν .

But taking $\xi > b$, the image of the doublet ν is $-\nu b^3/\xi^3$, distant b^2/ξ from B.

The two doublets together give the term

$$-4\pi \nu \frac{b^{m+2}}{\xi^{m+2}};$$

and it remains to evaluate

$$(-)^n 4\pi \sum \frac{d^{n-1}}{df^{n-1}} \left(\frac{b^{m+2} \nu}{\xi^{m+2}} \right),$$

where the summation extends to the doublet $\frac{a^{n+2} \mu}{n+1!}$ (or μ) and its images outside Y. For this doublet

$$\nu = \mu; \quad \xi = f.$$

For Q, the next image outside B,

$$\nu = \mu \frac{a^3 b^3}{(cf - b^2)^3}; \quad \xi = c - \frac{a^2 f}{cf - b^2}.$$

The succeeding image introduces a term of order c^{-12} compared with that due to μ ; we shall neglect this.

Making $f=c$ after all operations are over, we have

$$\begin{aligned} -\nu \iint P_m \phi_A dS_2 &= \frac{4\pi a^{n+2} b^{m+2} \mu r}{c^{m+n+1}} \left\{ \frac{m+n!}{m+1! \, n+1!} \right. \\ &\quad \left. + \frac{a^3 b^3}{2c^6} \left(1 + \frac{m+2 \cdot a^2 + n+2 \cdot b^2}{c^2} + \frac{p}{c^4} \right) + \dots \right\}, \end{aligned}$$

where

$$p = (m+2)(m+3)a^4 + 2(m+2)(n+2)a^2 b^2 + (n+2)(n+3)b^4.$$

It remains to find $\iint \phi_A P_n dS_1$, from which $\iint \phi_B P_m dS_2$ can be derived by symmetry.

The source μ at A contributes a constant, which we need not write.

The images P and Q contribute a term found by making

$$\nu = \mu b^3/f^3, \quad \xi = c - b^2/f.$$

The image R and its successor contribute only a small term; here ξ can be regarded as constant, since f only occurs in a term of order c^{-5} ; and ν is approximately $\mu a^3 b^6 c^{-6} f^{-3}$.

As far as terms of the order $c^{-(2n+10)}$ inclusive, $-u \iint P_n \phi_A dS_1$ is made up of the term

$$\frac{4\pi a^{2n+4} b^3 u^2}{c^{2n+4}} \left\{ \frac{1}{2!} + \frac{(n+2)^2 b^2}{3! c^2} + \frac{(n+2)^2 (n+3)^2 b^4}{4! 2! c^4} \right. \\ \left. + \frac{(n+2)^2 (n+3)^2 (n+4)^2 b^6}{5! 3! c^6} + \dots \right\},$$

due to the images P and Q, together with the term

$$\frac{2\pi a^{2n+4} c^3 b^6 u^2}{c^{2n+10}},$$

due to the image R.

By interchanging m and n , u and v , a and b , the remaining term on the right-hand side of (10) can be found.

If the vibrating spheres consist of liquid of density ρ' , the velocity-potential within X is $u P_n r^m / na^{n-1}$, and the kinetic energy of the sphere X is $\frac{2\pi \rho' a^3 u^2}{n(2n+1)}$. A similar expression holds for the other sphere.

When c is constant the principal term in the expression of the stress between the spheres varies as $c^{-(m+n+2)}$ or as $c^{-(2n+5)}$, or as $c^{-(2m+5)}$.

If u , v are simple harmonic functions of the time, the average stress between the spheres is to be found as before.

The case when $m=n=1$ has been discussed by Mr. Hicks (*loc. cit.*); for all other values of m and n the centres of the spheres are at rest.

X. On Transient Electric Current produced by suddenly twisting Magnetized Iron and Nickel Wires. By H. NAGAOKA, *Rigakusi, of Imperial University, Tokyo* *.

[Plate II.]

IN a recent number of Wiedemann's *Annalen*, Herr Zehnder† communicated the result of his experiments on the transient current produced by twisting magnetized iron and nickel wires, in which he finds the direction of current in nickel to be opposite to that in iron. The same result had been already known to me since July 1888. Being engaged in

* Communicated by Sir William Thomson.

† "Ueber Deformationsströme." Wiedemann's *Annalen*, Bd. xxxviii. p. 68. This number reached me on 14th October, 1889.

the investigation of the effect of twist in the magnetization of nickel and iron, I tried some preliminary experiments on the transient current produced by twisting magnetized wires. Thereby I hoped to trace some connexion between the transient current thus observed and the reversal of polarity* produced by twisting magnetized nickel wire, which is at the same time subjected to longitudinal stress. Though nothing striking was obtained in this direction, results not hitherto made known by the researches of Matteucci† and Ewing‡ were obtained. The following is the description of the experiments made in July and September, 1888.

The wire to be examined was well annealed and hung in a magnetizing solenoid. The coil was 30 centim. long and wound in 12 layers of thick copper wire, giving a magnetizing field of 36·7 units for a current of one ampere. The upper end of the wire was held fixed, while the lower was attached to a twisting apparatus provided with a graduated circle and a pointer. The two extremities of the wire were electrically connected to a low-resistance ballistic mirror-galvanometer. The transient current was measured by the first swing of the galvanometer. The deflexion was read after suddenly twisting the wire between two extreme limits of twist. Generally, it was after a number of twistings in both ways from the initial position of no twist, that the transient current settled to its final value.

Since the present investigation was undertaken with a view to ascertain the relation, if such exists, between this transient current and the reversal of polarity, the effect of longitudinal stress on the transient current was also looked into, as this played an important part in producing the reversal mentioned.

A nickel wire 30 centim. long and 0·5 millim. in radius was treated in the way above mentioned, the angle of twist amounting to 60° in both directions from the initial position of no twisting. The first experiment was performed under no longitudinal stress; the transient current produced by suddenly twisting the wire in various magnetizing fields was measured, the field being gradually increased from 0 to 110

* See "Effects of Torsion and Longitudinal Stress on the Magnetization of Nickel," Journ. of the Coll. of Science, Imp. Univ., Japan, vol. ii., or Phil. Mag. Feb. 1889; and also "Effect of Twist on the Magnetization of Iron and Nickel," Journ. of the Coll. of Science, vol. iii. At the end of the latter paper a short sketch of the results on the transient current is given.

† See Wiedemann's *Electricität*, Bd. iii. § 771.

‡ Proc. Roy. Soc. vol. xxxvi. 1884.

C.G.S. units (July 5, 1888). The following Table gives the readings of the first swing in different magnetizing fields:—

Nickel wire ($r = \cdot 5$ millim., $l = 30$ centim., $\tau = \pm 60^\circ$).

Unloaded.

\oint .	Reading of ballistic galvanometer.	\oint .	Reading of ballistic galvanometer.
$\cdot 21$	7	13.8	149
$\cdot 34$	15	19.9	151
$\cdot 71$	26	31.7	152
1.14	45	40.7	149
2.01	85	48.8	145
3.63	107	61.0	142
4.74	122	75.6	136
6.82	135	110.0	124
9.95	144		

The result is shown graphically in Plate II. fig. 1. Examining the curve we see that the current increases rapidly in low magnetizing fields; but as the magnetizing force becomes greater the increase takes place very slowly, passes a maximum, and begins to diminish nearly in a straight line.

On loading the wire and going through the same series of operations, the following readings of the deflexion were taken:—

Nickel wire ($r = \cdot 5$ millim., $l = 30$ centim., $\tau = \pm 60^\circ$).

Loaded 3 kgs.

Loaded 6 kgs.

\oint .	Reading of ballistic galvanometer.
$\cdot 71$	3
1.0	8
3.6	30
6.8	64
10.0	98
19.9	140
31.8	154
41.0	159
49.1	161
60.6	160
83.0	158

\oint .	Reading of ballistic galvanometer.
1.1	7
3.6	16
7.4	35
16.8	87
24.1	129
31.8	146
40.7	155
51.0	165
68.7	168
85.8	167

The above readings are plotted in fig. 1, from which we see that although the essential form of the curve is not

changed by loading, the maximum current is increased. At the same time, the point at which the current passes a maximum is shifted towards stronger field. The loading does not produce any remarkable change in the transient current.

Similar series of experiments were performed on an iron wire 1.02 millim. thick and 30 centim. long (July 8, 1888). The following Table gives the readings taken in different magnetizing fields :—

Iron wire ($r = .51$ millim., $l = 30$ centim., $\tau = \pm 60^\circ$).

With no load on.

Loaded 6.4 kgs.

\mathfrak{H} .	Reading of ballistic galvanometer.
.34	18
1.1	55
1.8	92
3.6	109
4.7	114
6.8	108
10.0	103
20.1	74
31.8	53
41.0	44

\mathfrak{H} .	Reading of ballistic galvanometer.
.34	45
1.0	21
2.1	36
2.8	40
4.7	47
7.9	50
10.0	49
19.2	39
31.0	30
41.0	24

These and two others are shown graphically in fig. 2. A glance at these curves will show that the transient current at first increases rapidly as the field is increased, but soon reaches a maximum and then begins to diminish gradually. The application of longitudinal stress diminishes the current, while at the same time the maximum point is transferred towards higher magnetizing field.

Comparing the results obtained for nickel and iron, we notice a peculiar difference in the behaviour of these two metals. The current which is produced by suddenly twisting the wire in the magnetizing field is, in the first place, opposite in direction. The direction* of the current in nickel is such that, the twist being applied like a right-handed screw, the current flows from south to north. In iron it is from north to south. This singular fact was also noticed later by Herr Zehnder.

In the experiments hitherto described the magnetizing force was gradually increased, and the transient current produced by suddenly twisting the wire at different magnetizing

* See Note by Sir W. Thomson appended to this paper.

fields was observed. There we see that both in iron and nickel the first increase of the field gives rise to rapid increase of the transient current. In unstretched iron this current attains its maximum strength at a field of about 5 C.G.S. units. It then gradually decreases as the field is further increased. In nickel of nearly the same length and thickness as the iron this current attains its maximum value very slowly, so that it is difficult to ascertain precisely the strength of the field at which this point is reached. Moreover, this maximum, though not very distinct, occurs at a magnetizing field far greater than that for iron.

The application of longitudinal stress produces opposite effects in the transient current in iron and nickel. The transient current due to sudden twist in iron always decreases when acted upon by pulling stress, whereas in nickel it diminishes in low magnetizing field, but beyond a certain strength of the magnetizing force the current in stretched wire attains greater value than in the unstretched wire. Thus the maximum transient current in nickel increases with the amount of longitudinal stress.

The effect of pulling the wire changes, not only the amount of the current, but also the strength of the field at which the current attains its maximum value. The effect is similar in both iron and nickel, although the amount of shifting of maximum in the former is less than in the latter.

That the transient current produced in twisting iron wire reaches a maximum was first noticed by Professor Ewing; the method of procedure in his experiments being different from the one here described. He measured the current produced in a twisted wire by reversing the direction of the magnetizing force. In the present experiment the current produced by twisting the wire was observed. In one of Professor Ewing's experiments the transient current induced in an iron wire 34 centim. long and 1 millim. thick, and twisted through 60°, passed a maximum when the strength of the field was 15 or 16 C.G.S. units. The wire used in the present experiments cannot be much different from the one used by Professor Ewing. The transient current attained its maximum value for $H=5$. Whether the discrepancy between these two results is due to the quality of iron wire or to the difference in the method of procedure, is a question not easily to be decided.

A simple glance at the results hitherto obtained will show the similarity between the phenomenon here investigated and the Wiedemann effect. In the latter phenomenon the twist produced by magnetizing a circularly magnetized iron wire

is in opposite sense to that of nickel. Moreover the maximum twist in iron occurs in lower magnetizing field than that in nickel. These facts closely resemble the transient current produced by twisting nickel and iron wires. In fact Professor J. J. Thomson* has shown that the existence of the Wiedemann effect necessarily leads to the production of electromotive force by twisting a longitudinally magnetized wire. According to Shelford Bidwell† the Wiedemann effect in iron comes out in the same sense as in nickel when the magnetizing force is sufficiently increased. In order to see if there is any such similarity in these two phenomena, the transient current produced in high magnetizing field was examined.

Using the dynamo current, a magnetizing force of 300 or 400 units was easily obtained, and observations made with nickel wire are as follows (July 11, 1888) :—

Nickel wire ($r = \cdot 5$ millim., $l = 30$ centim.).

§.	Reading of ballistic galvanometer.	Twist.	
333	55	$\pm 60^{\circ}$	Under no load.
409	43	± 60	"
333	66	± 60	Loaded 3 kgs.
321	81	± 60	" 6 "
333	91	± 90	" 6 "

The transient current in nickel wire diminishes with the increase of the magnetizing force, as will be seen from the readings given above. Even in a field of 300 units, the loading produces increase of the current-strength.

With an iron wire 1·46 millim. thick and 30 centim. long, and twisted through 60° , the following readings were taken:—

§.	Reading.	Twist.
202	3·5	$\pm 60^{\circ}$
338	Inappreciable.	± 60
404	"	± 60
550	"	± 60

* See 'Application of Dynamics to Physics and Chemistry,' p. 70.

† Phil. Mag. September 1886.

The current produced in iron wire caused an appreciable deflexion of the galvanometer in a field of 200 units, and in the *same* direction as for lower fields. On raising the magnetizing force to 300 or 400 units, no current of measurable strength was produced. If the transient current becomes reversed in direction, the deflexion of the galvanometer becoming null in field of 300 units, an appreciable throw of the mirror should have been noticed in the opposite direction for $\mathfrak{H}=400$ or $=500$. Judging from the fact that no such change is observed, it seems probable that the current never becomes reversed even by further increasing the magnetizing force. The current thus appears to decrease asymptotically with the increase of magnetizing field. Professor Ewing also arrived at a similar conclusion.

The next point to be investigated was the effect of various amounts of twist on the transient current. There are two ways of examining the proposed problem. We may either vary the magnetizing field, while the twist is kept constant, and work out separately for different twists; or we may keep the magnetizing force constant while the twist is made to vary.

Both these cases have been tried. The first case was tried with iron wire of different thicknesses, and the result is shown graphically in fig. 3. The thinner wire was twisted through $\pm 15^\circ$, $\pm 20^\circ$, $\pm 30^\circ$, and $\pm 60^\circ$ (September 25, 1888). All these curves show that the current increases with the increase of twist. The maximum point remains nearly in the same magnetizing field for three small twists, but is shifted toward stronger field as the twist is increased. A similar tendency will also be noticed in the curves obtained for the wire of .73 millim. radius (September 22, 1888). The rate of decrease of the current as the field is increased becomes more rapid for the thick than for the thin wire.

Similar experiments performed on nickel wire of 0.43 millim. radius are shown graphically in fig. 1 (dotted lines). They are for the twists of 30° and 60° respectively. The increase of the current with the increased twist is quite apparent, but nothing definite can be said about the shifting of the position of maximum transient current. After a certain strength of the magnetizing force, the current increases so gradually, that without very delicate measurement it is difficult to know exactly where the maximum point is situated.

To examine how the current increases with the increase of twist, I had recourse to the second mode of investigation, *i. e.*,

Phil. Mag. S. 5. Vol. 29. No. 176. Jan. 1890. K

changing the amount of twist while the magnetizing force is kept constant.

The following Table gives the readings of the first swing, in weak as well as strong magnetizing fields.

Iron Wire ($r = \cdot 51$ millim.,
 $l = 30$ centim., $\mathfrak{H} = 2\cdot 45$).

τ .	Reading of ballistic galvanometer.
10	4.0
15	15.9
20	30.2
25	43.4
30	52.9
40	63.5
50	68.7
60	71.7
70	70.7
80	70.3
90	68.8

Iron Wire ($r = \cdot 73$ millim.,
 $l = 30$ centim., $\mathfrak{H} = 112$).

τ .	Reading of ballistic galvanometer.
15	3.7
20	6.1
25	7.1
30	9.1
40	13.2
50	16.1
60	19.0
70	21.5
80	23.4
90	24.7
100	24.3

The results of these and other experiments (September 22–26, 1888) are plotted in fig. 4.

Examining the curves obtained in weak magnetizing fields, we notice that the transient current increases with the increase of twist at first very rapidly, but after passing the “Wendepunkt” becomes very gradual. The current ultimately attains maximum strength, and then begins to diminish. In a strong magnetizing field the current is greatly diminished, and the curve becomes less steep. The increase goes on slowly with the increase of twist up to the maximum. Comparing the results obtained in different magnetizing fields, we notice that the twist for which the current is maximum becomes greater as the magnetizing force is increased. In fact the maximum for the wire of radius $\cdot 73$ millim. occurs when the twist is about $\pm 60^\circ$ for $\mathfrak{H} = 5\cdot 0$, while for $\mathfrak{H} = 112$ the twist of 100° is barely sufficient to make the current reach the maximum strength.

With nickel wire treated in the same way as above, the following readings were taken (October 1, 1888):—

Nickel Wire ($r=0.43$ millim., $l=29.4$ centim., $\mathfrak{H}=27.5$).

τ .	Reading of ballistic galvanometer.	τ .	Reading of ballistic galvanometer.
10°	13	50°	74
15	21	60	77
20	35	70	79
25	46	80	79.5
30	57	90	80.3
40	69	100	80.5

The result is plotted in fig. 4 by dotted lines, where the ordinates are measured upwards for convenience, although they are actually below, as in fig. 1. The general feature of the curve does not differ much from those obtained for iron wires. The increase of the current beyond the "Wendepunkt" takes place very slowly, but it does not reach a maximum even for the twist of 100° . If the maximum exists, it must be for a larger angle of twist.

It has been remarked by Professor Ewing that the production of the transient current is a natural consequence of Sir William Thomson's * discovery, that æolotropic stress gives rise to an æolotropic magnetic susceptibility in iron. By twisting the wire, the lines of induction, originally parallel to the axis, are changed into helices. The component in the plane section, normal to the axis of wire, induces the transient current above described. Taking the Villari reversal into consideration, he also explained why the transient current in iron does not flow in the opposite direction, when the magnetizing force is greatly increased.

The development of æolotropic susceptibility by twisting the nickel wire, will similarly explain the production of transient current in that metal. The stress on twisting the wire is equivalent to extension and compression along lines perpendicular to the radius, and inclined at 45° to the normal plane section. According to the experiments of Sir William Thomson † and Professor Ewing ‡, the susceptibility in iron

* Phil. Trans. 1878; or 'Mathematical and Physical Papers,' vol. ii.

† *L. c.*

‡ Phil. Trans. 1888.

is, by stretching, rendered less in the elongational line than in lines perpendicular to it. The result is that the lines of induction of twisted wire are no longer straight, but are changed into helical lines. They are inclined toward the direction of relatively increased magnetic susceptibility. The direction of the transient current will be thus determined by that of *compression*. In iron, on the contrary, the direction of the current is that corresponding to *stretching**. Consequently, the direction of the current in nickel must be opposite to that in iron.

In nickel there is nothing corresponding to Villari reversal in iron. The magnetization of nickel is always diminished by stretching, while it is increased by compression. The consequence is that the circular component of the lines of induction is always on the increase as the twist becomes greater. This will account for the reason why the transient current does not reach a maximum even when the angle of torsion amounts to 100°.

Further investigations on the subject will be published in the Journal of the College of Science, Imperial University, Japan.

Tokyo, Oct. 17, 1889.

[*Note on the Direction of the Induced Longitudinal Current in Iron and Nickel Wires by Twist when under Longitudinal Magnetizing Force.* By SIR W. THOMSON.

To avoid circumlocutions suppose the iron or nickel wire to be vertical, and the magnetizing current to be in the opposite direction to that of the motions of the hands of a watch held with its face up. The undisturbed magnetization is downwards†. Now suppose a right-handed twist to be

* For explanation of this see Note by Sir W. Thomson added below.

† Much of circumlocution is avoided, and of clearness gained, throughout dynamics and physics, by introducing the substantive noun *ward* (as has been done by my brother Prof. James Thomson in his lectures on Engineering, and in lithographed sheets put into the hands of his students, in the University of Glasgow) to signify *line and direction in a line*;—that which is represented ordinarily by a barbed arrow. Taking advantage of this usage I now define the ward of magnetization as the ward in which the magnetizing force urges a portion of the ideal northern magnetic matter or northern polarity. By northern polarity, I mean polarity of the same kind as that of the earth's northern hemisphere. It is that which is marked *blue* by Sir George Airy to distinguish it from southern magnetic matter or southern polarity, which he marked *red*. According to a usage condemned 300 years ago by Gilbert, but not yet quite dead, English instrument-makers still sometimes mark with an N the true south pole, and with an S the true north pole, of their steel bar-magnets. All confusion due to this unhappy mode of marking magnets is done away with by Sir George Airy's red and blue.

given to the wire. Its elongational spiral is right-handed, and its contractional spiral is left-handed. If the substance is iron, the lines of magnetization become left-handed spirals; if nickel, right-handed. Now a downward current, in the downwardly magnetized wire, would, by the superposition of circular magnetization in the direction opposite to that of the hands of a watch, cause the lines of magnetization to become left-handed spirals. Hence the sudden right-handed twist induces in iron a current upwards, in nickel a current downwards. Thus we have the following simple specification for the directions of the induced longitudinal currents in the two substances, without reference to "up" or "down."

From any point, P, on the surface of the wire, draw same-wards parallels to the current in the nearest part of the magnetizing solenoid, and to the direction of the induced longitudinal current. Draw a helix through P making an acute angle with each of these lines. This helix is of same name as the elongational helix for iron, and as the contractional helix for nickel.—W. T., Dec. 21, 1889.]

XI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxviii. p. 493.]

November 20, 1889.—W. T. Blanford, LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. "On the Occurrence of the Striped Hyæna in the Tertiary of the Val d'Arno." By R. Lydekker, Esq., B.A., F.G.S.

2. "The Catastrophe of Kantzorik, Armenia." By Mons. F. M. Corpi.

The village is 60 kil. from Erzeroum, and 1600 metres above sea-level. Subterranean noises and the failure of the springs had given warning, and on 2nd August last part of the "Eastern mountain" burst open, when the village, with 136 of its inhabitants, was buried in a muddy mass.

The author described the district as formed of Triassic, Jurassic, and Cretaceous strata, subsequently broken up and torn by granitic, trachytic, and basaltic rocks, which overlie or underlie the Secondary rocks, according to the nature of the dislocation.

The flow was found to have a length from east to west of 7-8 kil., with a width ranging from 100 to 300 metres, and the contents were estimated at 50,000,000 cubic metres. It appeared as a mass of blue-grey marly mud, which, after the escape of the gases, solidified at the top; the inequalities projected to the extent of 10 metres. The site of the village was marked by an elevation of the

muddy mass, some of the débris of the houses having been carried forward. The lower part of the flow was still in a state of motion, and carried forwards balls of marly matter.

It was difficult to approach the source of this flow on account of the crevasses in the side of the mountain. An enormous breach served as the orifice for the issue of the mud, which emitted, it was said, a strong odour. The violent projection of this marly liquid and "incandescence" (?) mass had carried away a considerable portion of the flanks of the mountain, whose débris might be recognized on the surface of the flow by the difference of colour. Great falls were still taking place, throwing up a fine powder which rose into the air like bands of smoke. There were also fissures and depressions of the ground at other localities in the neighbourhood.

3. "On a new Genus of Siliceous Sponges from the Lower Calcareous Grit of Yorkshire." By Dr. G. J. Hinde, F.G.S.

December 4.—W. T. Blanford, LL.D., F.R.S., President,
in the Chair.

The following communications were read :—

1. "On the Remains of Small Sauropodous Dinosaurs from the Wealden." By R. Lydekker, Esq., B.A., F.G.S.

2. "On a peculiar horn-like Dinosaurian Bone from the Wealden." By R. Lydekker, Esq., B.A., F.G.S.

3. "The Igneous Constituents of the Triassic Breccias and Conglomerates of South Devon." By R. N. Worth, Esq., F.G.S.

During the investigation several hundred fragments were examined, the largest occurring at Teignmouth, between which place and Dawlish the breccias are most varied in composition, and contain the greatest proportion of granitoid rocks. The igneous fragments were thus divided :—I. Granites ; II. Felsite group : *a*, non-schorslaceous, *b*. schorslaceous ; III. Andesitic group ; IV. Miscellaneous. Of these, including in all 76 varieties, I., II. *b*, and IV. are plainly of Dartmoor origin in gross, the schorslaceous and contact-altered rocks having belonged to the outer or to an upper zone ; III. can for the most part be identified with the *in-situ* "felspathic traps" of the neighbourhood. The non-schorslaceous division of II. differs but little from Dartmoor elvans ; some may have been surface-portions of felsitic dykes, or even fragments of felsitic lavas. The igneous fragments of the breccias, as a rule, are not much altered structurally ; they are of local origin.

The large blocks indicate the vicinity of high land abutting on a shore-line. Of this high land Dartmoor is a relic. The transporting power of water was perhaps supplemented by a glacial climate and volcanic activity. De la Beebe considered that igneous action accompanied the earliest "red-rock" deposits. The "felspathic traps" are known to be both antecedent to and contemporaneous with the breccias, and there is evidence which points to their being comprised within the period of igneous activity represented by the Dartmoor elvans. The author says that there is a preponderance of

volcanic over plutonic igneous rocks, and thinks that the existing remnants of "felspathic traps" are not sufficient to supply the quantity. He suggests that they must have come from an upper portion of Dartmoor.

In conclusion, the author considered that he has shown that the igneous materials are of local origin, and that they consist of granites, felsites, and volcanic types, ranging from andesites to basalts; that the few igneous fragments not hitherto assigned to *in-situ* rocks are yet of a similar character; that the conditions under which the "felspathic traps" occur *in situ* lead to the inference that they are volcanic phenomena which probably represent the final phase of the igneous activity of the Dartmoor region. Lastly, he expresses his opinion that the elevation of Dartmoor and the associated igneous phenomena took place at a period not earlier than the Permian.

4. "Notes on the Glaciation of parts of the Valleys of the Jhelam and Sind Rivers in the Himalaya Mountains of Kashmir." By Capt. A. W. Stiffe, F.G.S.

After referring to the previous writings of Messrs. Lydekker, Theobald and Wynne, and Col. Godwin-Austen, the author gave an account of his observations made during a visit to Kashmir in 1885, which appeared to him to indicate signs of former glaciation on a most enormous scale.

A transverse valley from the south joins the Sind valley at the plain of Sonamurg, and contains glaciers on its west side. These, the author stated, filled the valley at no remote period, and extended across the main Sind valley, where horseshoe-shaped moraines, many hundred feet high, occurred, and dammed the river, forming a lake of which the Sonamurg plain was the result. The mountains which originated the above glaciers were described as being cut through by the Sind river, and the rocks of the gorge were observed to be striated, whilst rocks with a moutonnée appearance extended to a height of about 2000 feet.

The whole of the Sind valley was stated to be characterized by a succession of moraines through which the river had cut gorges, whilst the hillsides were seen to be comparatively rounded to heights of 2000 feet or more.

The author had also formed the opinion that at Baramulla the barrier of a former lake occupying the Kashmir valley was partly morainic, before reading Prof. Leith Adams's view of the glacial origin of some of the gravels of this point.

The whole valley of the Jhelam from this point to Mozufferabad showed extensive glacial deposits, which had been modified by denudation and by the superposition of detrital fans, widely different in character from the glacial deposits. Below Rampoor the valley was thickly strewn with enormous granite blocks resting upon gneiss, and the author believed that they had been transported by ice.

In conclusion, it was noted that the existing torrential stream had further excavated the valley since Glacial times and, in places, to a considerable depth.

XII. *Intelligence and Miscellaneous Articles.*

THE MAGNETISM OF NICKEL AND TUNGSTEN ALLOYS.

BY JOHN TROWBRIDGE AND SAMUEL SHELDON.

Introductory.

THE fact that different kinds of steel, alloyed in small proportions with tungsten or wolfram, and magnetized to saturation, increase in specific magnetism*, has long been known. Whether the same effect would result from the use of nickel alloyed with tungsten has never been investigated. This paper has for its object a partial answer to the query. It was instigated by Mr. Wharton, proprietor of the American Nickel Works, whose chemist, Mr. Riddle, kindly prepared the alloys which have been employed. These alloys were in two groups. The first, received in November 1888, consisted of three bars of the same shape, one being of pure nickel and the other two having respectively 3 and 4 per cent. of tungsten in alloy. These bars were rolled from cast ingots, which were toughened by the addition of magnesium after Fleitmann's method, the magnesium being added just before pouring. They were hot when rolled. The one of pure nickel was afterwards planed into regular shape. Those containing tungsten were too brittle to allow of this manipulation. They were, however, of sufficient regularity to permit accurate measurements. This group contained also an octagonally shaped bar with 8 per cent. of tungsten, which was prepared like the others, and was afterwards ground into shape.

The second group, received in May 1889, contained bars which were simple castings, made without the addition of magnesium, and consisted of pure nickel and alloys with 1, 2, 3, and 6 per cent. of tungsten. All the bars in this group were extremely hard and brittle. In making them tungsten oxide, of weight calculated to yield the desired percentage of tungsten in the resulting alloy, was placed with adequate carbon in the bottom of a graphite crucible and covered by the proper weight of pure grain nickel. All was then covered with borax, the lid of the crucible was placed on, and the crucible was heated until reduction and fusion were completed.

Method.

As the suspected influence of the tungsten would be to affect the magnetic moment of the bars, these were magnetized to saturation and their specific magnetism then determined, *i. e.*, the magnetic moment for each gram of metal.

The magnetization was effected by placing the bars separately in a hollow coil whose length was 15 centim. and outside and inside diameters respectively 6 and 3 centim. It consisted of 6 layers of wire having 63 turns each. A dynamo current of 40

* Journ. Chem. Soc. 1868, xi. p. 284, says 300 per cent.

amperes was then sent through the coil for one minute, and the circuit then broken and the bars removed.

For the determination of the magnetic moment, use was made of a reflecting-magnetometer, and deflexions were observed with a telescope and scale at a scale-distance of 100 centim. Measurements of the horizontal intensity, H , of the earth's magnetism were first made. The results from these determinations by means of the first and second Gauss arrangements were, respectively,

$$H = 0.1724 \text{ Centim. G. S.}$$

$$H = 0.1720 \quad , ,$$

The freshly magnetized bars were then placed in the second Gauss position relative to the magnetometer, and the angular deflexion determined. The specific magnetism, S , was then calculated by the formula

$$S = \frac{r^3 H \tan \phi}{m},$$

where

r = distance from bar to magnetometer = 72.68 centim.;

H = earth's horizontal intensity = 0.1722;

m = mass of the bar;

ϕ = angular deflexion of magnetometer.

Results.

The mean results of two sets of observations on Group I., and also upon a similar bar of soft tool steel, are given in the following table:—

Group I.

Composition.	Size in cms.	Mass in grams.	$S[\text{Cm.}^{\frac{1}{2}} \text{G.}^{-\frac{1}{2}} \text{Sec.}^{-1}]$.
Pure Nickel	$18 \times 2.7 \times 0.65$	284.5	1.23
Ni + 3 p. c. W	" " "	286.5	10.60
Ni + 4 p. c. W	" " "	283.5	10.40
Tool Steel	$15 \times 2.5 \times 0.5$	159.5	7.46
Ni + 8 p. c. W	(13×1.5) Octagonal	144.0	5.25

Group II., of cast bars, gave the following results:—

Group II.

Composition.	Size in cms.	Mass in grams.	$S[\text{Cm.}^{\frac{1}{2}} \text{G.}^{-\frac{1}{2}} \text{Sec.}^{-1}]$.
Pure Nickel	$18 \times 1.8 \times 1.6$	459	1.05
Ni + 1 p. c. W	" " "	455	1.92
Ni + 2 p. c. W	" " "	454	1.70
Ni + 3 p. c. W	" " "	463	1.75
Ni + 6 p. c. W	" " "	465	1.15

The bars of both groups were, subsequent to the above observations, completely demagnetized, and then freshly magnetized. New determinations gave the same results as before. The demagnetization was accomplished by placing the bars inside two coils, which were traversed by currents from an alternating dynamo. The coils were then slowly drawn apart, and the bars maintained at a position central between them. After treatment

in this manner, they showed no appreciable deflexion when placed in position relative to the magnetometer.

The results tabulated indicate that tungsten greatly increases the magnetic moment of nickel, if the alloy be forged and rolled, but, on the other hand, has but small influence if it be simply cast. Furthermore, changes in the amount of tungsten do not appear to cause corresponding changes in the magnetic properties.

To see whether the remarkable effect in bars 2 and 3, as compared with bar 1, of Group I., was owing to some molecular condition of their surfaces induced by rolling, two bars from the same steel, one rolled and the other pressed, were magnetized and then measured. The ratio of the specific magnetism of pressed to rolled was as 9 to 5, the rolled having the smaller amount. The existing difference, in this case, is probably owing to a difference in hardness rather than to any molecular condition of the surfaces.

The specific magnetisms of all the bars are small when compared with good steel magnets. Kohlrausch says that good magnets of common form should have $S=40$. The bar of ordinary tool steel, however, retained but 7.46. Still it was soft, and by tempering would doubtless have doubled this value.

If forged nickel and tungsten can be made to maintain a specific magnetism of 10, it will form a useful addition to the resources of physical laboratories. From the high polish of which it is susceptible and its freedom from damaging atmospheric influences, it will be most happily suited for the manufacture of mirror magnets where magnetic damping is to be employed.—Silliman's *American Journal of Science*, December 1889.

NOTE ON THE APPLICATION OF HYDRAULIC POWER TO MERCURIAL PUMPS. BY FREDERICK J. SMITH, M.A., MILLARD LECTURER, TRINITY COLLEGE, OXFORD.

In vol. xxv. p. 313, 5th series, *Phil. Mag.*, a description is given of the application of hydraulic power to the working of mercurial pumps.

Since the paper was written the author has ceased to use rubber tubes, and has, in their place, introduced flexible tubes made of steel. As the alteration has proved itself to be satisfactory, and may be of use to those who work with mercurial pumps, or similar apparatus, he ventures to add this note.

The steel tube is made by the Flexible Metallic Tube Co. in the form of a hollow screw, or tube on which a screw-shaped indentation has been impressed. The outcome of the construction is that while the tube is under a great pressure it is quite flexible, behaving itself in much the same way as a strong rubber tube, with the advantage over the latter of being durable when subject to, constant motion. Several pieces of tube, made of steel and bronze, have been tested up to 200 lb. per square inch, without showing any signs of being injured. These have been used in the laboratory for connecting together vessels which are subject either to a

high pressure or a vacuum. Sometimes the tube has been used for liquids which act upon the metal it is made of; when this has been the case, a rubber tube has been threaded through the metal tubes, so as to form a protective lining.

ON EVAPORATION AND SOLUTION AS PROCESSES OF
DIFFUSION. BY PROF. J. STEFAN.

In a paper published in 1873 the author described experiments which he made on evaporation from narrow tubes. Those observations led to the law that the velocity of evaporation is inversely proportional to the distance of the surface from the open end of the tube. The application of the theory of the diffusion of gases to this process led to the same law, and at the same time furnished a complete determination of the velocity of evaporation, which renders it possible to calculate the coefficient of diffusion of vapours. These experiments have been extended by Winkelmann to several series of liquids, and have been used to determine the coefficients of diffusion of their vapours.

Similar experiments to those on evaporation may be made on the solution of solids in liquids. A rectangular prism of rock-salt was made: its height was 30 millim., and the two other dimensions were 7 and 9 millim. Glass plates were cemented by Canada balsam to the bottom and sides, so that only the top surface of the prism was free. In one of the glass plates a scale is etched. If the prism, with its top upwards, is immersed in a large vessel of water, its solution takes place from the top and the process can be observed on the scale. After 1, 4, 9, 16 days the solution had extended to 6.3, 12.6, 18.8, and 25 millim. These depths are as the square roots of the times. Hence for this process the law holds that the velocity of the solution is inversely proportional to the distance of the rock-salt surface from the open end of the prism.

If such a prism is dipped with the free surface downwards, the solution proceeds with almost uniform velocity. In one hour 17.1 and in $1\frac{1}{2}$ hours 25.6 millim. were dissolved. A prism of a metre in magnitude requires for its solution from upwards 70 years, and downwards $2\frac{1}{2}$ days; the former times increase with the magnitude in a quadratic, and the latter in simple ratio.

Experiments of the first kind may be used for investigating the diffusion of salts through their solvents. It is necessary for this to represent the process in a form which can be calculated from the theory of diffusion. This gives a new method for determining the coefficient of diffusion of salts. The method is not restricted to such bodies as can be obtained in large crystals. If a uniform mixture or a magma is formed of the powder and its saturated solution, and if a graduated tube is filled with it, the progress of the solution can be as well observed by it as with a prism of rock-salt. The law in this case is the same as in the former case, though the absolute value of the velocity with which the plane of separation of the solution and of the magma moves downwards

is greater, and the more so the smaller the quantity of undissolved salt in the magma.

The mathematical part of the paper consists of four divisions. In the first, the equations of the theory of diffusion of gases are developed. In the second, they are applied to evaporation. The solution of this problem in the former paper was only an approximate one, yet quite sufficient for calculating the experiments. In the present paper the exact solution of the problem is communicated. Their establishment forms a fresh application of the equations which the author has developed in the theory of the formation of ice. In the third section the differential equations of the diffusion of gases are transformed into the equations which serve for calculating the diffusion of liquids. The last section contains the applications of these equations to the calculation of experiments on diffusion.—*Wiener Berichte*, Nov. 21, 1889.

ON THE CHANGES OF TEMPERATURE RESULTING FROM THE
TORSION AND DETORSION OF METAL WIRES. BY DR. A.
WASSMUTH.

In the year 1878 Sir W. Thomson (*Phil. Mag.* vol. v. p. 19) deduced from the mechanical theory of heat the principle that a twisted wire must become cooled when the torsion is suddenly carried further.

In the above research it is proved for iron, brass, and particularly for steel that the phenomenon in question actually occurs; and the opposite one on detorsion, that the cooling or heating increases with the angle of rotation, and that the change of temperature observed for a steel wire agrees very well with the calculated one.

In these experiments thermoelements were soldered to six steel wires connected with each other by pieces of wood, and slightly stretched horizontally, in such a manner that this wire arrangement could both be stretched and twisted. It was possible in this way to compare the very small changes of temperature on torsion and detorsion with the much larger ones due to stretching, and which indeed can be done in two ways. For the cooling θ which occurs on the torsion of a wire of length l from the angle w_0 to w_1 it was calculated

$$J \frac{m}{l} c \theta = t \frac{n}{10^4} \frac{E}{2(1+\mu)} \frac{\pi}{2} r^4 \frac{1}{2} \frac{w_1^2 - w_0^2}{l^2},$$

in which m was the weight, r the radius, $\frac{E}{2(1+\mu)}$ the modulus of torsion, $\frac{n}{10^4}$ its relative decrease with the absolute temperature t , c the specific heat of the wire, and J the mechanical equivalent of heat. There was thus obtained for θ ,

Calculated $195 \cdot 10^{-5}$ of a degree Centigrade;

Observed $191 \cdot 10^{-5}$ " " "

Several further experiments likewise showed agreement with what has been said.—*Wiener Berichte*, Nov. 7, 1889.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

FEBRUARY 1890.

XIII. *The Pressure-Variations of certain High-Temperature Boiling-Points.* By CARL BARUS*.

1. **I**N the following pages I briefly describe a practical method for the calibration† of thermocouples by aid of boiling-points, and then apply it in measuring the vapour-tensions of zinc, cadmium, and bismuth. During the course of the work a neglected principle of Groshans‡ is advantageously employed. I must state at the outset that it is not the object of this paper to furnish accurate values for boiling-points. My purpose is to investigate the probable nature of the relation of boiling-point to pressure, throughout very

* Communicated, with the permission of the Director of the U.S. Geological Survey, by the Author.

† The literature of the subject, which is very voluminous, may be omitted here, because I give a full account of it in the Bulletin of the U.S. Geological Survey, no. 54, pp. 23 to 55, 1889. Among recent authors H. Le Chatelier (*cf. Bull. Soc. Chim. Paris*, n. s. xlv. p. 482, 1886; *ibid.* xlvii. pp. 2, 300, 1887; *C. R.* cii. p. 819, 1886; *Journ. de Physique*, vi. p. 23, 1887, and elsewhere) is particularly active in promoting thermoelectric high-temperature research. In the 'Bulletin' I describe methods of standardization by aid of boiling-points (pp. 84 to 125), and by direct comparison with Deville and Troost's porcelain air-thermometer (pp. 165 to 248). I also submit an independent method of my own, based on the high-temperature viscosity of gases (pp. 248 to 306). Experiments made conjointly with my colleague, Dr. William Hallock, on capacious high-temperature vapour-baths, are discussed in another part of the 'Bulletin' (pp. 56 to 83).

‡ Groshans, Pogg. *Ann.* lxxviii. p. 112, 1849.

Phil. Mag. S. 5. Vol. 29. No. 177. Feb. 1890. M

wide ranges of temperature, with the hope of stimulating speculations on the subject, somewhat more rigorous than that of Groshans (§16). It is clear that if a law can be found by which the normal (76 cm.) boiling-point of a substance can be predicted from an observed low-pressure boiling-point, then a more complete knowledge of high temperature boiling-points can be arrived at than is now available. More than this: by varying pressure, boiling-points of different metals may be made to overlap each other. Hence a thermocouple calibrated as far as the boiling-point of zinc, for instance, may be used to measure a low-pressure boiling-point of bismuth (say); and the couple then may be further calibrated by the normal boiling-point of bismuth, predicted by aid of the law in question. The process may obviously be repeated. The couple whose calibration interval has been enlarged in the manner given may now be used to fix the low-pressure boiling-point of some other suitable metal, and then in turn be further calibrated by aid of its boiling-point. The limit of such a method is the fusibility of platinum. The fact that at high temperatures the vapours to be used will be either monatomic or diatomic enhances the interest of the project (*cf.* Biltz and V. Meyer, § 15, below).

2. The platinum/iridio-platinum thermocouple used in this work had on another occasion* been tested for polymerization anomalies, by minute comparison with the porcelain air-thermometer, and between about 400° and 1300° none were found. The alloy contained about 20 per cent. of iridium. Unfortunately I could not avail myself of the former air-thermometer comparisons, nor was it expedient to repeat the work. M. Le Chatelier† rejects the iridio-platinum couple because of irregularities of the kind referred to. Dr. Hallock and I have also found them pronounced in other iridio-platinum couples‡. In the present couple slight irregularities between 350° and 450°, equivalent to about 5°, had to be allowed for. When the range of temperatures is very large, the Avenarius-Tait equation is insufficient; but this equation subserves a good purpose when interpolations between two fixed temperature-data are called for, the data lying anywhere on the scale, but not too far apart.

Apparatus.

3. Boiling-points below 500° may be studied in a closed glass tube, *a a a*, fig. 1, within which a thin-walled tube, *d d d*, open at both ends, passes coaxially quite through. In the

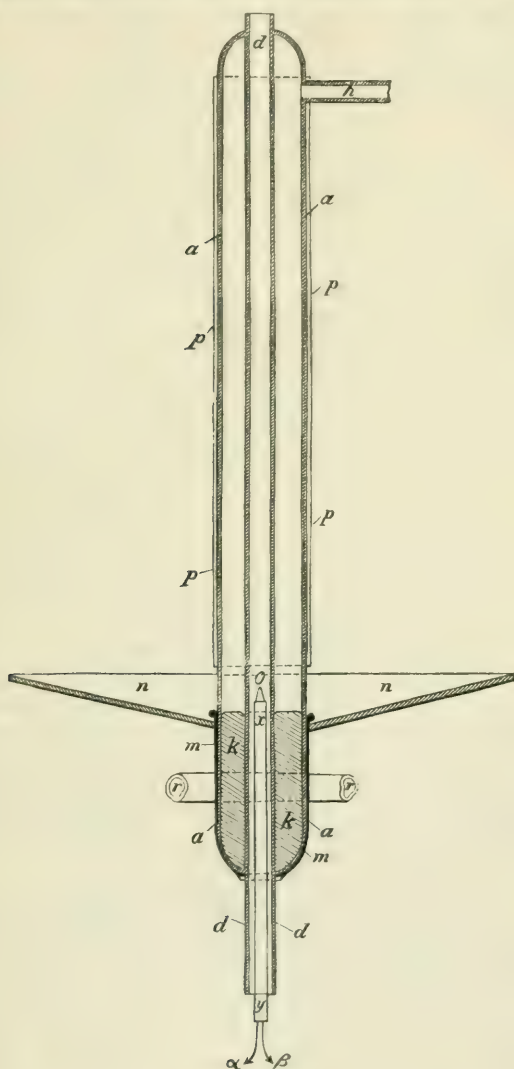
* Bull. U.S. Geol. Survey, no. 54, p. 208 *et seq.*, 1839.

† Le Chatelier, *l. c.*

‡ Bull. U.S. G. S. no. 54, pp. 80, 114 *et seq.*, 1889.

bottom of the annular space between the tubes, the ebullition liquid, *k k*, is placed, and it is heated by Wolcott Gibbs's ring-

Fig. 1.—Longitudinal section of boiling-point tube. Scale $\frac{1}{2}$ to $\frac{1}{3}$.



burner, *r r*. A conical asbestos screen, *n n*, protects the upper part of the tube from direct radiation. Other screens

and jackets, *pppp*, are suitably added. The upper end of the tube, *aaaa*, is in communication with the air-pump, through the lateral tubulure *h*. Finally, to obviate breakage, the lower end of the tube is protected by a metal jacket, *mm*.

The thermocouple to be calibrated, $\alpha o \beta$, is introduced into *dd* from below, and raised until the junction *o* is slightly above the plane of ebullition of the liquid, *kk*. The upper part of the tube is closed with asbestos wicking (not shown) as far down as *o*. The wires of the couple pass through parallel canals in a rod of fire-clay, *xy*, and are thus well insulated. The boiling-points of most organic substances, mercury, sulphur, &c., are conveniently obtained in this way, provided the pressure be not too low (§§6, 7). The vacuum boiling-point of cadmium is also easily reached. In general, boiling may be kept up for any length of time—often a great desideratum. If the substance *kk* be very volatile, like methyl alcohol for instance, a condenser is added at *h*. By using diphenylamine and a thickly jacketed tube, I found no difficulty in keeping the whole column (30 cm. long) at a practically constant temperature (310°). When normal boiling-points (76 cm.) only are wanted, it saves breakage to leave the tube *aaaa* open above, and to close it with a cork*.

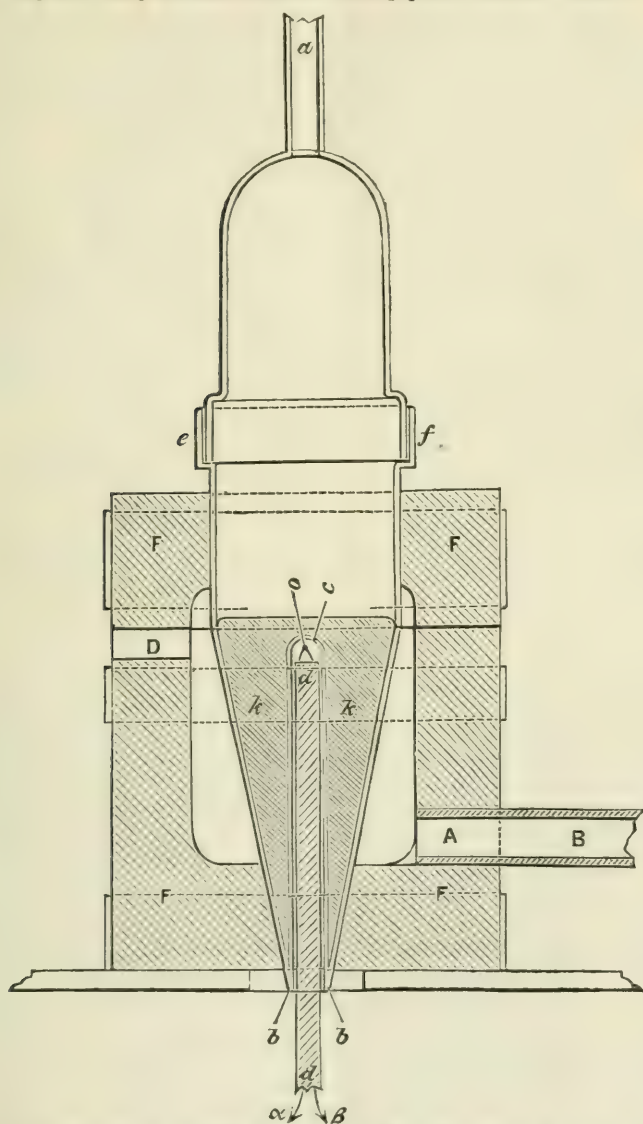
4. In the case of boiling-points above 500° it is more convenient to use glazed porcelain or fire-clay crucibles, resembling *aebbf a*, fig. 2. In some forms I run the central tube *bcb* quite through the crucible, so as to project at the lid; but this makes the apparatus very much more fragile. Usually the closed tube *bcb* of the figure is satisfactory. The ebullition liquid is shown at *kk*, and the thermocouple $\alpha o \beta$ is again introduced from below. *dd* is the fire-clay insulator. To vary the pressure under which boiling takes place, the tube *a* is connected with an air-pump. Finally a tight joint at *ef* is secured by calking with asbestos fibre, and then filling up the annular space left above the asbestos with fusible metal.

The crucible *aebbf a* is surrounded by a small furnace of Fletcher's composition, *FFFF*, and heated by one or more blast-burners, *AB*. Products of combustion escape at *D*. If the flame impinges directly on the cold crucible the latter is apt to get broken; but such breakage may be prevented by surrounding the crucible with a conical shell of asbestos. Unfortunately crucibles can be used but once, for they are

* For details of construction, manipulation, degree of constant temperature, burner, insulators, &c., see the 'Bulletin' (54) cited, pp. 80 to 89, 94 to 97.

usually fractured by the cone of solidified metal *k k* on heating a second time. Any single ebullition, however, may be

Fig. 2.—Longitudinal section of boiling-point crucible. Scale $\frac{1}{2}$.



prolonged almost indefinitely, that is half a day or more. I found no serious difficulty in obtaining vacua of two or three

millimetres, at extreme white heat. The crucible must be well glazed internally; and it is probable that the work will be facilitated by using tubular forms made in a single piece, *i. e.* without the joint *ef*. In such a case the crucible *ebbfa* may be reduced in size, and placed wholly *within* the furnace, the tube *a* leading out of it. The charge will then be more effectually heated. A charge of granulated metal is easily introduced through *a*. When normal boiling-points are wanted, smaller crucibles of fire-clay are preferable*.

5. The thermoelectric powers can best be measured by a null-method, in which the thermoelectric constants are expressed in terms of a given Latimer-Clark's cell. Recalibration is then rarely necessary, and calibrations made at different times may be compared. But the adjustments and computations, if they occur in great number, are inconvenient. In this respect the torsion-galvanometer† offers decided advantages. I constructed an apparatus of this kind in which the thermoelectromotive forces are directly expressed in terms of the twist of a platinum fibre.

The description of the galvanometer must be omitted here. Its chief points are an astatic, aperiodic magnetic system, the needles (two bundles of four each) of which are of glass-hard steel, consecutively annealed at 100° in order to secure stability both against changes of temper and of magnetization‡. The instrument is 135 cm. high, and is read off by the observer standing. The magnetic moment of each needle (10 cm. long) being intense, only a moderately thin platinum fibre (.018 cm.) suffices; and as the needles are brought back to the fiducial zero of the instrument by torsion of the wire, the directive effect of the terrestrial or local magnetic fields is quite eliminated. The torsion-circle is sharply divided in single degrees; the fractions are read off by telescope and scale, a mirror being attached to the needle. Both telescope and scale are compendiously fixed to the galvanometer. Thermoelectromotive forces are therefore expressed in terms of a fixed standard, the torsional rigidity of the platinum wire, and hence they are comparable even after the lapse of time. Any temperature between 100° and intense white heat may be measured without further adjustment. These desiderata, added to convenient manipulation and the durability

* For details, particularly with regard to superheating, see Bull. U.S. G. S. no. 54, pp. 89 to 94.

† The priority of adapting Coulomb's torsion-balance for thermoelectric measurement is due to Schinz (Dingler's Journal, clxxv. p. 87, 1865; *ibid.* clxxix. p. 436, 1866). Cf. Bull. U.S. G. S. no. 54, p. 48.

‡ Cf. Strouhal and Barus, Wied. Ann. xx. p. 683, 1880; or Bull. U.S. G. S. no. 14, chap. vi. 1885.

of the instrument against wear and tear, constitute the advantages of the galvanometer constructed.

M. Le Chatelier * recommends the Deprez-D'Arsonval galvanometer.

From what has been stated, if D be the twist corresponding in a given instrument to the temperatures T and t of the junctions of the given thermocouple, $D = a(T - t) + b(T^2 - t^2)$. Again, if $d = a(t - 20) + b(t^2 - 20^2)$, it follows that

$$D_{20} = D + d = a(T - 20) + b(T^2 - 20^2).$$

Hence a small table for d is to be computed, for temperatures t between 10° and 35° . A short preliminary calibration suffices for the purpose. In this way the observer may at once deduce D_{20} from D , where D_{20} is a function of T , the temperature of the hot junction only. By aid of known melting-points (Le Chatelier), or boiling-points (water, mercury, sulphur, cadmium, zinc, bismuth), the quantity D_{20} may then be graphically constructed as a function of T . Intermediate points between two consecutive boiling-points, T_1 and T_2 , are filled in by using the constants of the equation

$$D_1 - D_2 = a(T_1 - T_2) + b(T_1^2 - T_2^2).$$

From a chart of this kind, the temperature T corresponding to any twist D is taken with facility.

Observations.

6. In the above apparatus the normal boiling-point (76° centim.) of mercury is sharply determinable; but there is considerable difficulty in determining the low-pressure boiling-points. Unless the heat be regulated to a nicety, the lower layers boil under the pressure of the upper layers. Again, since the agitation of the mercury nearly ceases in approximate vacua, a flame of reasonable intensity presupposed, the rate of evaporation is much decreased. In the case of a liquid of small specific heat, of relatively large cohesion, films of which do not adhere uniformly to glass, it is therefore to be suspected that both liquid and vapour will be superheated in relatively very large degree at low pressures. If the flame be intensified so as to produce violent ebullition at low pressure, the liquid can be superheated to such an extent that its direct radiation on the junction of the thermocouple may increase its temperature as much as 10° above the boiling-point.

* Le Chatelier, *Seizième Congrès Soc. Industr. du gaz*, 1888.

Accordingly I was not surprised to find that the temperatures obtained in the static method by Regnault, Hagen, Hertz, Ramsay and Young*, are as a rule decidedly below the corresponding boiling-points of the present dynamic method. It is only by taking great pains in the adjustment of burner and apparatus, that my temperatures began to coincide with those of Regnault. But this nice adjustment introduces arbitrary conditions; hence the low-pressure boiling-points of mercury are to be rejected. At high pressures the unsatisfactory circumstances mentioned fall away, and the rate at which boiling-point changes with pressure is very much reduced. Fig. 3, § 15, will show the difficulties which I strove to overcome; but as my data, even in the final work, are not of exceptional accuracy, I will omit them here.

7. The behaviour of sulphur is peculiar. On removing pressure to about 1 centim., the substance passes into the treacle state, and the full ebullition observed under atmospheric and other pressures changes into sticky frothing. Exact temperature data cannot therefore here be expected. The following Table is an example of the earlier results obtained, P being the pressure in centimetres of mercury, and T the corresponding boiling-point in degrees Centigrade.

TABLE I.—Boiling-points of Sulphur.

P.	T.	P.	T.	P.	T.
centim.	° C.	centim.	° C.	centim.	° C.
0	218	4.8	298	21.2	374
0	205	7.0	316	39.8	410
2.4	263	11.2	337	76.0	448

The next Table contains results of a later date, in which much care was taken to guard against the difficulties mentioned. D_{20} , the twist in degrees of arc, has been added to show the sensitiveness of the torsion-galvanometer.

* Ramsay and Young, Journ. Chem. Soc. xlix. p. 37, 1887; Landolt and Boernstein's Tables, p. 58 (Berlin, Julius Springer, 1883). I may advert in passing to the discussion between Ramsay and Young and Kahlbaum. The former, corroborating Regnault's law, maintain that vapour-tensions, whether obtained by the static or the dynamic mode of measurement, are identical. Kahlbaum claims to have found a difference, and he is sustained by O. Schumann (*Chem. Ber.* xviii. p. 2085, 1885). Both authors make use of Landolt's vapour-tensions.

TABLE II.—Boiling-points of Sulphur.

P.	D. ₂₀	T.	* T.	P.	D. ₂₀	T.	* T.
centim.		° C.	° C.	centim.		° C.	° C.
75.84	27.976	446	448	6.55	18.30	316	324
55.36	26.57	428	429	4.06	16.80	295	305
55.41	26.59	429	429				
54.75	26.49	427	428	75.87	27.999	448	448
48.30	25.87	420	422	30.69	23.65	389	396
47.78	25.64	416	421	30.70	23.65	389	396
37.59	24.51	402	407	13.01	20.18	342	354
37.57	24.39	399	407	12.93	20.18	342	354
28.67	23.44	386	393	5.61	17.28	302	317
28.80	23.51	387	394	5.91	17.51	305	320
20.68	22.23	370	376	6.14	17.62	306	321
20.70	22.25	370	376	3.29	15.55	278	295
14.37	20.76	349	358	3.44	15.51	277	297
14.49	20.73	348	359	1.67	11.21	228	275
11.15	19.66	335	346	1.39	11.85	†223	266
11.25	19.77	336	347	1.05	11.33	†215	260
6.11	18.05	313	321	0.75	10.76	†206	252
6.35	18.20	315	323				

* Extrapolated by Regnault-Bertrand's formula.

† Sulphur sticky.

These results agree fairly well with those of the earlier Table. I have added values of T extrapolated graphically § from Regnault's data by aid of the Dupré-Bertrand equation (§ 12) $\log p = 19.10740 - 4684.49/\theta - 3.40483 \log \theta$, which holds between $\theta = 663$ and $\theta = 843$ absolute degrees Centigrade. It will be seen by comparison of my values with the data predicted by this formula that there is much error at low pressures.

8. Table III. contains data of four sets of experiments with zinc. The first of these were made in the glass tube (fig. 1) at low pressure. Although in this case there was profuse volatilization, I did not observe any ebullition. In the table the result marked * is the only datum of this work inserted. Change of temperature with pressure was not obvious. The remaining data of this part of the table are legitimate and were obtained from crucible experiments (fig. 2). The criterion of boiling-point is change of temperature with pressure. In the second and third parts of the Table, I aimed at greater accuracy. Each of the values given is a mean of two or three distinct measurements. † refers to low position, and ‡ to a high position of the thermocouple in the central tube *bcb*, figure 2.

§ I computed the inferior prolongation of the curve, and plotted the results. From the chart the values of T were taken correct to 1 degree.

TABLE III.—Boiling-points of Zinc.

P.	T.	P.	T.	P.	T.
centim. *1.0	° C. 582	centim.	° C.	centim.	° C.
		4.2	710	2.6	675
		3.5	699	6.7	731
4.0	710	2.8	684	15.8	792
6.5	732	6.2	736	26.4	833
9.6	757	9.9	758	37.5	864
10.1	772	16.6	802	47.3	884
15.6	785	26.4	838	57.0	904
27.1	837	36.8	863	65.4	916
34.5	857	47.7	884	77.1	933
42.5	873	55.7	900		
53.5	897	65.3	914		
76.4	933	77.3	928		
		77.3	922		

9. Table IV. contains three sets of experiments with commercial cadmium, the first of which were made in the glass tube. Ebullition in vacuum was obvious; but inasmuch as the limit of heating-power of the ring-burner is not much above 500°, the remaining thermal data are too low.

The experiments of the 2nd and 3rd parts of this table were made in the porcelain crucible. They are legitimate; change of temperature taking place with every change of pressure. I was unable to make the crucible satisfactorily tight. Mean values of somewhat varying pressure had to be inserted. Again, cadmium is more easily superheated than zinc, so that the present temperatures are probably high. Repetitions of the experiment failed from breakage of the crucible.

TABLE IV.—Boiling-points of Cadmium.

P.	T.	P.	T.	P.	T.
centim.	° C.	centim.	° C.	centim.	° C.
.00	444	26.2	702	6.3	606
2.75	526	29.2	706	8.4	622
5.25	549	35.5	724	22.6	686
7.70	562	38.1	729	27.4	704
		48.9	745	34.2	722
2.2	549	51.7	750	51.0	752
2.5	552	62.4	760	56.3	760
2.6	565	64.4	766	63.6	770
3.2	574	65.6	766	65.6	772
7.5	620	75.6	772	75.5	786
10.5	639	75.6	770	75.5	788
15.7	667	75.6	774	75.5	781
18.9	681				

10. Table V. contains results for bismuth. In the first part of the Table temperature does not change with pressure. Hence a boiling-point is not reached. In the second part of the Table temperature certainly oscillates with pressure. Hence the temperature corresponding to the lower values of pressure (3 centim. to 4 centim.) are boiling-points. The temperature corresponding to the higher values of pressure (9 centim. to 10 centim.) are below the corresponding boiling-points; for I found that on further increasing pressure the temperature did not increase. The temperatures observed are therefore the limit of the heating-power of the furnace. At least 5 minutes must be allowed for each observation. The top of the crucible should be filled with asbestos to diminish loss of heat by radiation.

TABLE V.—Boiling-points of Bismuth.

P.	T.	P.	T.	P.	T.
centim.	° C.	centim.	° C.	centim.	° C.
2.6	1152	3.2	1199	9.5	1236
5.8	1164	8.6	1211	3.4	1207
2.6	1165	9.7	1207	4.0	1217
8.1	1182	3.2	1206	9.7	1260
8.8	1186	3.7	*12 2	3.4	1206
2.7	1183	4.2	1215	3.9	1221
9.8	1194	3.7	1247	9.6	†1258
2.4	1186	3.9	1213	3.3	1215
		3.4	1204	4.2	1233

* Flame intensified; B.P. criterion satisfied.

† Limit of burner-power.

11. In the above Tables I. to V., the criterion of boiling-point has been change of temperature with pressure. When this was not observed the data were rejected. The method of obtaining low boiling-points from liquids is *à priori* objectionable, because of the liability to superheating. In special measurements made with zinc*, however, I found the error thus introduced to be negligible. There seems to be less superheating in case of metals and high temperatures, supposing the temperature of the environment to be reasonably near the boiling-point (say 200° or 300° above it). In case of bismuth and metals of higher boiling-points, the difficulties of experiment are such that I do not think a capacious vapour-bath for low pressures feasible.

Experiments with antimony failed from breakage of crucible.

* Bull. U.S. G. S. no. 54, pp. 108, 109, 1889.

Inferences.

12. Equations expressing tension of saturated vapour in terms of temperature have been invented in great number. Among them the simple form of Magnus and the more elaborate exponential due to Biot, and applied by Regnault, are given in most text-books. A remarkably close-fitting exponential is investigated and tested by Bertrand*. Quite recently M. Ch. Antoine† has devised and applied a new form. Following the early suggestions of Bertrand‡ and of J. J. Thomson§, I have used the equation of Dupré||,

$$\log p = A - B/\theta - C \log \theta, \quad . \quad . \quad . \quad (1)$$

where p and θ are corresponding values of pressure and boiling-point in absolute degrees Centigrade, and A , B , and C are constants. Equation (1) has been independently interpreted by Thomson. Its immediate meaning appears more clearly in the differential form

$$\begin{aligned} \text{or} \quad dp/d\theta &= -p(C/\theta - B'/\theta^2), \\ d\theta/dp &= (\theta^2/p) (1/B'(1 - \theta C/B')), \end{aligned}$$

with reference to which it is to be observed that C/B' is a small quantity.

Applying equation (1) to the results of the Tables I. to V., I found the following set of constants by direct computation.

TABLE VI.—Constants for Boiling-point and Pressure.

Metal.	A.	B.	C.
Sulphur *	-35.969	- 366.1	-13.066
Cadmium	-30.567	+ 1391	-11.180
Zinc	+42.265	+11435	+10.022

* When these constants were computed, the data of Table I. only were in hand.

The results are irregular, even as to sign. Other direct methods gave similarly irregular constants, which need not

* *Thermodynamique*, pp. 154 to 162 (Paris: Gauthier-Villars, 1887).

† *C. R.* cvii. pp. 681, 778, 836, 1888.

‡ *L. c.* pp. 90 to 102.

§ 'Application of Dynamics, &c.,' pp. 158 to 161 (Macmillan, 1888).

|| *Théorie mécanique de la chaleur*, pp. 96 to 120 (Paris: Gauthier-Villars, 1869).

be entered here. Little can be learned from them, as might have been expected. To get comparable values for the constants of a complex equation, the data must either be very fine or in great number.

13. Bearing in mind therefore that it is my object to detect possible relations, and that my high-temperature boiling-points are necessarily somewhat crude, I will facilitate computation by observing that in Dupré's data the prevailing value of A is between 15 and 20. Assuming $A=20$, the following set of constants were obtained, in which, of course, there is greater uniformity. Water is added from Dupré and Bertrand.

TABLE VII.—Constants for Boiling-point and Pressure.

Substance.	A.	B.	C.
Water *	19.324	2795	3.868
Sulphur	20	4379	4.217
Cadmium	20	7467	3.643
Zinc	20	8433	3.603

* Bertrand (*l. c.* p. 93) inadvertently puts $A=17.44324$, in which case, however, pressures are measured in atmospheres instead of millimetres of mercury, which is his usual standard. The same constant is repeated by J. J. Thomson.

14. From an inspection of Table VII., I was led to suspect better agreement in making C constant throughout, and A variable. This step is further suggested by assuming, conformably with the indications of Table VII., that for any two substances S and S' the boiling-points θ and θ' , corresponding to a given pressure p , will follow the relation $B/B' = \theta/\theta' = 1/n$, where n is constant for the given pair of substances. This is virtually the principle of Groshans, and postulates a fundamental equation of the form (1), from which all others are derived by substitution as follows:—

$$\log p = A - B/\theta - C \log \theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= A - nB/n\theta - C \log n\theta + C \log n,$$

$$= A' - B'/\theta' - C \log \theta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The constants of Table VIII. are obtained by supposing C to be constant for all the substances. As to a choice of

value, I noticed that the mean C of Table VII. is nearly the same as Bertrand's C for water. Hence it was selected.

TABLE VIII.—Constants for Boiling-point and Pressure.

Substance.	A.	B.	C.
Water	19.324	2795	3.868
Sulphur	19.776	4458	3.868
Cadmium	20.63	7443	3.868
Zinc	20.98	8619	3.868
Bismuth	21.51	12862	3.868

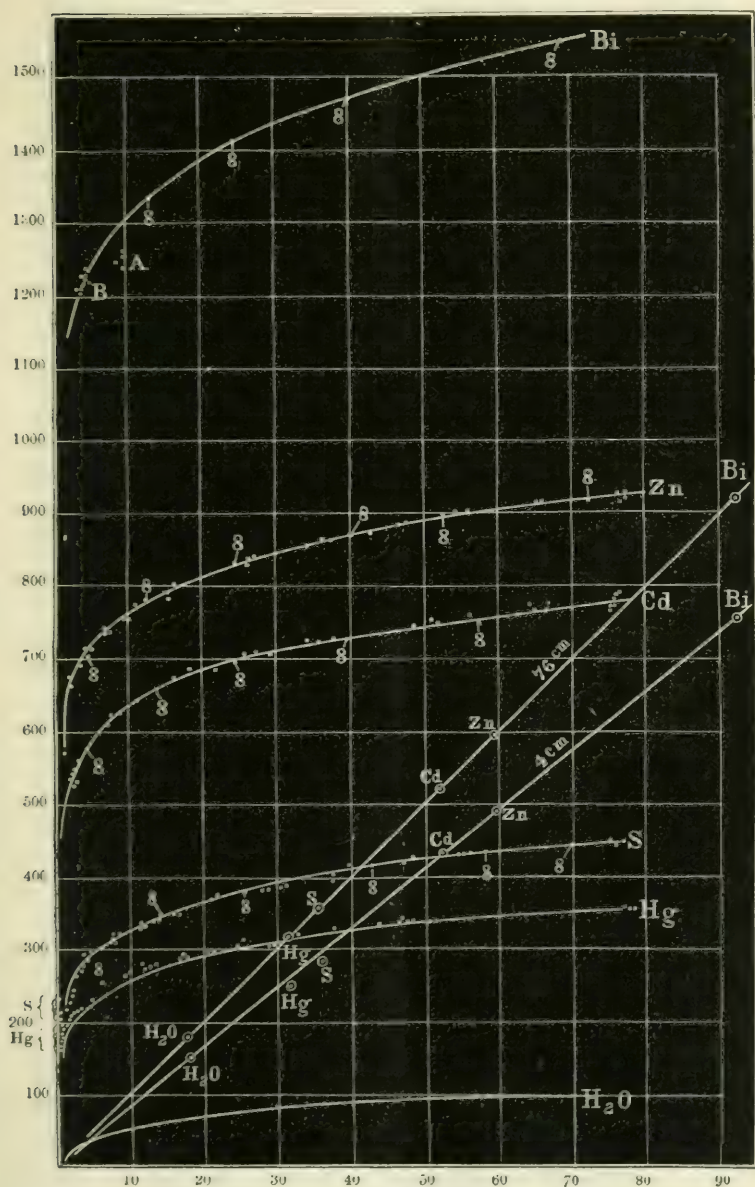
These constants could be improved by successive trials; but further work would be wasted. The data for sulphur in Table II. (7 cm. to 76 cm.), which coalesce pretty well with Regnault's data (27 cm. to 388 cm.), suggest a calculation of constants including both sets of results. I will supply this elsewhere, since it is not essential here. Extrapolation by aid of the sulphur constants, Table VIII., does not reproduce Regnault's high-pressure data.

15. In order to exhibit the point of view taken, it is necessary to plot the results graphically. This is done in fig. 3, in which the abscissæ are pressures in centimetres of mercury, and the ordinates boiling-points in degrees Centigrade. In the case of mercury I have inserted the vapour-tension curve of Regnault, showing that, conformably with § 6, it is uniformly lower than the present data. Points computed by the constants of Table VIII. are marked. It appears from an inspection of the chart that the agreement between observed and computed results is nearly in keeping with the errors of observation.

The results for bismuth are particularly interesting. Unfortunately it was impossible for me to calk the crucible quite tight. Hence the low-pressure boiling-point of bismuth does not overlap the normal boiling-point of zinc, which limits the calibration interval of the thermocouple. The chart shows the interval of extrapolation to be about 270°. This makes the bismuth results less certain; and the normal boiling-point of bismuth deduced by Groshans's principle, 1550°, is possibly too high. Carnelley and Williams *, using

* Carnelley and Williams, Journ. Chem. Soc. London, xxxv. 1879, p. 565.

Fig. 3.—Chart showing the relation of Boiling-point and Pressure, for Water, Mercury, Sulphur, Cadmium, Zinc, and Bismuth, and the relation of corresponding Boiling-points at 76 centim. and 4 centim.



a fusing-point method, give 1450° as the maximum temperature for boiling bismuth, which means, however, that it is short of the melting-point of nickel taken at 1600° (Van der Wyde). In my own experiments* with a Fletcher furnace like fig. 2, I signally failed to boil bismuth† in a number of trials, in which I used three blast-burners. The boiling-point criterion in the present results is beautifully exhibited. When pressure increases, the group of points B on the chart passes into group A; hence the group B are boiling-points. When pressure increases further, the group A do not increase in temperature; hence the group A are not boiling-points‡. The zinc and the later sulphur results are most satisfactory. Irregularities in the cadmium observation for the higher pressures I attribute to leakage of the crucible (§ 9).

The straight lines running obliquely across the chart exhibit the approximate truth of Groshans's principle. The abscissæ are boiling-points, θ , at 76 cm., the ordinates boiling-points at 76 cm. and 4 cm. respectively, all expressed in double absolute degrees Centigrade; *i. e.* the chart shows the variations of $\theta/2$. Mercury and sulphur fall below the line of proportionality. Inasmuch as it is possible that the 4-centimetre data for zinc and cadmium are slightly superheated, the general agreement of data may be better than it here appears. It is by aid of this diagram that the bismuth constants in Table VIII. were computed.

16. Bertrand computes the constants of Dupré's formula for 16 substances, and shows its admirable agreement with observed data throughout. The constants in such a summary vary largely: A between 4 and 21 (pressures being expressed in centimetres of mercury); C between -9 and $+5$. In any such grouping of constants as I have very roughly attempted, the agreement of the formula with facts would therefore be lost. It is worthy of remark, however, that in 10 of the 16 substances, A lies between 15 and 21.5, and in one half of the substances C lies between 3.2 and 4.2.

When, however, the errors left in any attempt to group the constants are considered, not so much with reference to the small range of temperatures of a single substance, but rather with regard to the relatively large range of tempera-

* Bull. U.S. G. S. no. 54, pp. 116-118, 124.

† In determining the vapour-density of bismuth, Biltz and V. Meyer heat bismuth up to 1700° (*Chem. Ber.* xxii. p. 725, 1889), but the temperature is purposely chosen high.

‡ Very interesting experiments on the volatilization of metals *in vacuo* and at low temperatures (Cd at 160° , Zn at 184° , Sb and Bi at 292° , Pb and Sn at 360°) are due to Demarcay, *C. R.* xcv. p. 183, 1882.

ture exhibited by the phenomena as a whole, and by a diagram such as fig. 3, for instance, then the errors in question assume much smaller importance. In the above pages I have presumed to believe that at the outset the wide temperature comparison is the one which ought *first* to be made, and some fundamental relation applicable to the whole range of temperature investigated. After this has been done, the said relation may be modified to suit the individual case.

I can state this more clearly as follows:—Groshans's derivation of his principle* is sufficiently simple. If vapours have identical coefficients of expansion, 1.273 say, and their densities be expressed relatively to the density at the normal boiling-point in each case, then the ratio of absolute boiling-temperatures corresponding to any two given pressures will be the same for all vapours. This inference is incorrect, just in proportion as the application made of the Boyle-Charles law is incorrect.

However, Dupré in deriving his formula makes virtually the same assumption†. Again, J. J. Thomson‡ introduces Boyle's law into the mean value of the Lagrangian function investigated for the occurrence of maximum vapour-tension; but since the form of an arbitrary function of temperature is here determined by experiment, the insertion of Boyle's law suffices Thomson's purposes. Following the model of his work, I hoped to find some suggestion as to a modification of Dupré's equation, such that it may be the outcome of an original type for all substances, by inserting Van der Waals's law instead of Boyle's law into the proper term. It seemed plausible that Dupré's equation could thus be corrected by aid of constants, a and b , the molecular interpretation of which has already been given by Van der Waals. Performing the operations, I find, rigorously,

$$\begin{aligned} R\theta \log \frac{\rho_0}{\rho} \frac{\xi - b\rho}{\xi - b\rho_0} = \\ - R\theta \left(\frac{\xi}{\sigma} \frac{\rho}{\xi - b\rho} - b \frac{\rho_0}{\xi - b\rho_0} \right) + \frac{a\rho}{\xi} \frac{\rho - \sigma}{\sigma} + (w - w') - \psi(\theta), \end{aligned}$$

an equation which, though capable of simplification, essentially involves ξ , and is therefore not suggestive.

Physical Laboratory, U.S. Geological Survey,
Washington, D. C., U.S.A.

* Somewhat similar approximate relations are investigated from Regnault's data by Dupré (*l. c.* pp. 115–117). Groshans used data for water and carbonic acid gas. An older principle due to Dalton (*Lit. Soc. Manchester*, v. p. 550) is incorrect. The work of Kopp and of Bartoli on corresponding boiling-points has special reference to volumes.

† Bertrand, *l. c.* p. 101.

‡ Thomson, *l. c.* p. 158.

XIV. *The Electrification of a Steam-jet.*
 By SHELFORD BIDWELL, M.A., F.R.S.*

THE boiler used in these experiments consists of a small tin bottle capable of holding about fifteen fluid ounces, which is supported upon a tripod above a Bunsen burner. Its neck is fitted with a cork, through which passes a glass tube $\frac{5}{16}$ in. in diameter, terminating in a nozzle with an opening of about $\frac{1}{16}$ in. At a point four inches above the cork, the tube is bent to an angle of 100 or 110 degrees, and the nozzle may be formed at a distance of five or six inches from the bend. In this case its direction will, of course, be nearly horizontal. When it is desired to have a vertical nozzle, the tube is again bent in an upright direction at a distance of not less than five inches from the first angle, the nozzle terminating two or three inches above the second bend. The nozzle is made by simply drawing out the tube to a point in a flame, and cutting off its end at the proper place.

I have given these dimensions in detail, not, of course, because they are absolutely the best possible, but in order that anyone who wishes to repeat the experiment may be enabled to obtain good results without trouble. The object aimed at is to keep the tube as free as possible from water, whether arising from ebullition or from condensation, so that the jet of steam may be regular and uniform ; at the same time, it is essential that the end of the nozzle from which the steam issues should not be directly above the gas-burner, or the experiment cannot succeed.

The tin bottle is charged with four ounces of water, and when it boils the burner is adjusted until the steam-jet is as vigorous as is possible consistently with steadiness ; if the ebullition is too violent, the water thrown up into the tube will produce jerks, masking the effect to be looked for.

The jet is most conveniently observed by means of its shadow projected upon a white screen. For this purpose a lime-light is desirable, but any good source of light may be employed. The shadow of the jet will be seen to be of feeble intensity and of a neutral tint ; the jet is, in fact, nearly transparent, and does not appear to exercise any selective absorption upon the light. If now a sharp point, or, better, a small bundle of points, in connexion with one of the terminals of an influence-machine (such as a Voss), is brought near the

* Communicated by the Physical Society : read December 6, 1889.

base of the jet, the machine being worked slowly, a startling change instantly comes over the shadow. It becomes dark and dense, at the same time assuming a marked orange-brown tint. By removing the point, or simply connecting it to earth, the shadow can be immediately caused to resume its original appearance, again becoming almost invisible. This operation may be repeated as often as desired, one of the most remarkable things about it being the extreme rapidity with which the changes are produced.

The point need not necessarily be directed to the origin of the jet; it is nearly as effective when placed in the steam at a distance of a foot or more from the nozzle; and in such a case the *whole* of the steam-jet is equally acted upon from its origin onwards, even when the direction of the point is the same as that of the jet. A ball may be used instead of a point, but it operates only when actually within the jet, whereas a point may be outside it. The effect may also be produced by directing the jet upon an electrified metal disk, supported at a considerable distance from the nozzle.

I have examined the absorption-spectrum of the steam-jet. When the jet is not electrified, its action upon the spectrum is small, the intensity of the whole being slightly diminished in an apparently equal degree throughout. Possibly the violet is dimmed in a somewhat greater proportion than the other colours. Electrification of the jet causes the violet to disappear completely, while the luminosity of the blue and the more refrangible part of the green is materially decreased. The orange and red are, I believe, quite unaffected.

From these facts it may be concluded that electrification causes an increase in the size of the water particles contained in the steam-jet. In the unelectrified condition the majority of these particles are small in relation to a wave-length of light; under the influence of electrification they become larger, and attain a diameter of something like a fifty-thousandth part of an inch.

The idea naturally suggests itself that the phenomenon may be of the same nature as that observed by Lord Rayleigh in the case of water-jets*. A stream of water issuing in a nearly vertical jet from a small orifice is found to break up into separate drops at a certain distance above the orifice. Under ordinary conditions these drops collide with one another, and, again rebounding, become scattered over a considerable space. But when subjected to the influence of an electrified body, as a rubbed stick of sealing-wax, brought near the point of resolution, the colliding drops no longer

* Proc. Roy. Soc. 1879.

rebound but coalesce, and the entire stream of water, both ascending and descending, appears to become coherent. Now it seems to me certain that the innumerable minute particles of water generated in the steam-jet, each consisting perhaps of only a few molecules, must necessarily come into frequent collision with one another; for we cannot suppose that they all travel with equal velocities and in exactly the same direction; and there is no reason why they should not behave just in the same manner as the larger drops of the water-jet, rebounding when they are not electrified, coalescing into larger drops when they are. It is true that the degree of electrification required to produce the phenomenon in the case of the steam-jet is apparently much greater than in the other, a rubbed stick of sealing-wax being altogether inoperative. Perhaps this is a consequence of the different sizes of the drops in the two cases. That the actual electrification of the particles in the steam-jet is really very small indeed, is proved by the fact that if two electrified steam clouds are generated in close proximity to each other, they exhibit little, if any, evidence of mutual repulsion when they are similarly electrified, or of attraction when their electrifications are of the opposite kind.

Lord Rayleigh shows cause for believing that if the electrifications of the drops in the water-jet were strictly equal, the phenomenon in question would not occur; and the reasons why they are not, in fact, equal would just as well apply to the case of the steam-jet. How unequal charges of electricity of the same name are operative in bringing about coalescence Lord Rayleigh does not explain, nor am I prepared to hazard a conjecture on the point.

Lord Rayleigh concludes his paper by referring to the importance of the investigation from a meteorological point of view. I may do the same. It seems certain that the steam-jet experiments go far towards explaining the cause of the intense darkness which is characteristic of thunder-clouds, as well as of the lurid yellow light by which that darkness is frequently tempered.

I had made the above described experiments and drawn the above stated conclusions concerning them, and had just requested the Secretary of the Physical Society to accept the present communication, when Prof. Silvanus Thompson, whose knowledge of scientific history is proverbially encyclopædic, was good enough to bring to my notice the fact that experiments upon the electrification of a steam-jet had been recently made in Germany by the late Robert Helmholtz. An account of these experiments, which are of the greatest

interest, is given in Wiedemann's *Annalen*, vol. xxxii. p. 1. The author appears never to have examined his jets by transmitted light, and makes no mention of the marvellous increase of opacity under electrification, to which I have called attention. His observations were all made against a *dark* background, the illuminating beam of light coming obliquely from the front, but shaded from the eyes. When the jet is electrified, he says, it is at once seen more clearly and sharply against the background; it also assumes diffraction colours, like those seen in strata of fog. Very strong electrification produces a deep blue colour, indicating the formation of very small mist drops. On slowly diminishing the electrification the blue tint at first becomes gradually paler, which points to the formation of larger drops; and it is then succeeded by tints of purple, red, yellow, green, and finally, when the discharge is very feeble, by pale blue tones again. Under certain circumstances all these several tints may be seen at once in different portions of the jet.

I, too, had observed these diffraction colours, which were sometimes very beautiful; but having convinced myself that they undoubtedly occurred at times when no electrical influence (that I knew of) was operating, I did not follow up the observation.

Helmholtz found that these condensation phenomena could be just as well produced by some other causes as by electrification, and especially by the agency of flame. All the exciting causes in question involve some continuous chemical action inside the steam-jet. He conjectures, therefore, that the sudden condensation may be due to molecular tremors or shocks, which upset the unstable equilibrium of the supersaturated vapour, just as a small disturbance will sometimes cause the sudden crystallization of a supersaturated saline solution; and after showing that chemical reactions may occur freely even outside the visible portion of a flame, he states his opinion that similar dissociations and recombinations take place among the molecules of the air affected by an electric discharge, as evidenced, for instance, by the formation of ozone.

A very striking illustration of the effect of combustion is afforded by holding beneath the jet a piece of burning touch-paper, made by soaking blotting-paper in a solution of nitrate of lead. The jet at once becomes quite as opaque as if electrical influence were employed, and the same hissing noise is also heard. The burning touch-paper suggested itself as more convenient than the actual flames used by Helmholtz for the purpose; for these cannot be brought underneath the jet without causing its immediate dissipation; and it is there-

fore necessary to hold them on one side, and direct their heated gases upon the jet by blowing or fanning.

After reading Helmholtz's paper it naturally occurred to me to try the effect of combustion upon the water-jet. In this case the objection to the use of an actual flame does not, of course, apply. I therefore introduced the flame of a Bunsen burner into the jet, and found that, if the air-holes were stopped up, and the flame thus rendered luminous, a decided effect was produced upon the jet. Often, indeed, it became just as completely coherent throughout its length as if it were electrified, though I have not yet succeeded in obtaining this result with perfect certainty; but in every case when the burner was held a little below the point of resolution, a considerable diminution of the scattering was observed. If the air-holes were opened and the flame made non-luminous, it failed to act in any way whatever upon the jet. It is to be remarked that Helmholtz found certain non-luminous flames (of which, however, a gas-flame was not one) to be devoid of influence upon the steam-jet.

Can the effect here also be due to electrification*? It can hardly be attributable to heating, because the flame of a Bunsen burner is certainly hotter when it is non-luminous than when it is luminous. On the other hand, it is known from many experiments that flame is electrified. If, for example, we place a luminous flame between the positive and negative ball-terminals of a Voss machine in action (the terminals being too far apart for sparks to pass), we find that the flame, or at least the upper part of it, is repelled by the positive and attracted by the negative ball. This seems to denote positive electrification of the flame.

In conclusion, it should be mentioned that Helmholtz suggests another hypothesis as an alternative to that of molecular shock, though he does not appear to attach much importance to it. It is that the electrical discharge, the flame or other exciting agent, whatever it may be, acts by introducing into the steam-jet minute particles of solid matter which serve as nuclei upon which the water-vapour may condense, as in Aitken's experiments on the formation of fog.

It is possible that several different causes may be competent to produce the condensation phenomena.

* In replying to the discussion which followed the reading of the paper, I suggested the possibility, which had occurred to me after it was written, that the flame might act simply by coating the separate particles of water with certain products of combustion, Lord Rayleigh having found that the addition of a little soap or milk to the water prevented the scattering. Perhaps the action of flame upon the steam-jet may be similarly explained.

XV. *The Geological Age of the Mountains of Santa Marta.*
By PROFESSOR HERMANN KARSTEN, M.D.*

THE Geological constitution of the mountain-mass of Sta. Marta has until recently remained quite unknown. It was only in consequence of my Report of 1852 upon "The neighbourhood of Maracaybo and the North coast of New Granada" (Karsten's *Archiv*, 1853), in which the geological age of these mountains was touched upon, and after the publication of the nearly simultaneous investigation of this region by Acosta (*Bull. Soc. Géol. Fr. sér. 2*, vol. ix. p. 396, June 1852), that these questions have been dealt with more in detail, both in my subsequent geological writings and in those of my successors.

Acosta, like myself, describes the Geological constitution of the Sierra Nevada de Sta. Marta as Plutonic, consisting of Granite, Gneiss, Syenite, Diorite, Eurite, &c., and of Porphyries traversed by veins of malachite. Neptunian strata, from which the age of the mountain-mass might be inferred, are not cited by Acosta; but he concludes, from the complete isolation of the massif, and from its East and West direction, that it existed long before the upheaval of the Cordillera, which runs North and South.

In my discourse upon "The Geological Constitution of New Granada" (*Ämtlicher Bericht der Versammlung der Naturforscher*, 1856, Vienna 1857) I also describe the Sierra Nevada de Sta. Marta in more detail as a distinct mountain-system which abuts with its south-eastern declivity upon the chain of Ocaña striking northward from Bogota, and by subsequent upheavals there was united therewith by means of a narrow and low connecting range (p. 81). This mountain-mass of Sta. Marta consists of alternating beds of crystalline rocks:—Granite, Gneiss, Protogine, Syenite, Hornblende-, Chlorite- and Quartz-schists,—which have a general strike from S.W. to N.E. In the periphery of this formation there are readily weathering Diorites, Porphyries, Syenites, Granites, &c. Towards the east and south-east beds of the Cretaceous formation bound these rocks, a continuation of those which compose the mountains of Ocaña (Perija). The lowest of these Neptunian beds is a red sandy laminated marl in which *Ammonites santafecinus*, D'Orb., occurs, and which alternates upwards with dark, bituminous limestones and siliceous schists containing Ammonites and *Luocerami*. These are covered by light-blue limestone-beds, in which *Ecogyra*

* Communicated by the Author.

Boussingaultii is plentiful. Upon the neighbouring south-east foot of the Plutonic rocks of the Sierra Nevada are deposited correspondingly stratified but unfossiliferous calcareous and aluminous rocks, in part crystalline and schistose.

In the valleys of this Cretaceous formation Tertiary strata are deposited up to at the outside 200 metres. These appear to be entirely wanting on the northern slope, where, however, according to the statements of the natives, limestone containing *Belemnites* occurs.

In opposition to Acosta, Hettner (Petermann's *Geographische Mittheil.* 1885, p. 92) concludes from the direction of the centre of the mountains from S.S.W. to N.N.E., that the mass is a continuation of the Central Cordillera, which is likewise furnished with a nucleus of Plutonic rock, and to which this line of strike under 8° N. lat. leads eastwards from the river Nechi; an opinion which is in harmony with the development of these Colombian mountain-chains as deduced by me from the nature of the Neptunian strata, although the contemporaneity of the two existing mountain-systems is not thereby proved.

In my Viennese address on New Granada (*Antlicher Bericht*, 1856), as well as in a more recent memoir on the Geology of the three northern Republics of South America*, in which I have brought together all that was observed by me in those countries, or that has been published by other travelers, I concluded that the mountains of Guiana are the central point of the different mountain-systems of Colombia, by which the direction of these mountain-chains was prescribed, having been elevated as the northern (Venezuela) and western (New Granada and Ecuador) borders of a great semicircular fissure which was formed in the solid crust of the earth around this primitive centre of upheaval, which, although it was not then recognizable in its whole extent by prominent mountain-masses, nevertheless traced out the direction of contemporaneous and subsequent eruptions.

The elevatory force which gave origin to this fissure in the periphery of the central mountain-mass already in existence appears to have acted from the east to the west and south, and indeed on the greatest scale in the north, gradually becoming weaker towards the south. On the contrary, the last considerable upheaval, that of the Tertiary epoch, followed the opposite direction; its greatest force was exerted in the south.

In the north the Plutonic mountain-chains which bound the

* *Géologie de l'ancienne Colombie Bolivarienne, Vénézuéla, Nouvelle Grenade et Ecuador.*—Berlin, Friedländer, 1886.

sea (Caracas, Sta. Marta) attained nearly their present elevation above the sea-level at their first upheaval, and were only a little further uplifted at the close of the Cretaceous* and Tertiary epochs, while the present Cordillera, extending southwards, remained still covered by the sea, and only attained its present form and elevation in this direction by means of the eruption of the trachytic masses and lavas, which occurred most powerfully in the south (Ecuador) and diminished gradually northwards (*Géologie*, p. 51).

The existing Sierra Nevada de Sta. Marta, like the mountains of Caracas, was already almost completely upheaved above the Cretaceous sea and still more completely above the sea of the succeeding Tertiary formation, as may be recognized from the conditions of stratification of the Neptunian deposits.

Whilst the Cordillera of New Granada and Ecuador, especially in its trachytic portions, is generally overlain nearly to the highest summits by strata of the Tertiary epoch, the two Plutonic mountain-masses of the north coast bear Tertiary deposits only up to small elevations (*Géologie*, pp. 12, 23, 52).

The two geographers, Simons and Sivers, the latest writers upon the Sierra Nevada, do not enlarge our knowledge of this geological question.

Simons (Proc. Roy. Geogr. Soc. 1879, 1881, and 1885), as the fruit of his investigations of the Sierra Nevada extending over several years, gives us an excellent geographical Map, the first and best of the original maps of this region founded upon personal surveys (Proc. R. G. S. 1881), as a completion of the admirable work of Codazzi, who, as is well known, perished under the deadly climate of the plains at the commencement of the survey of this province.

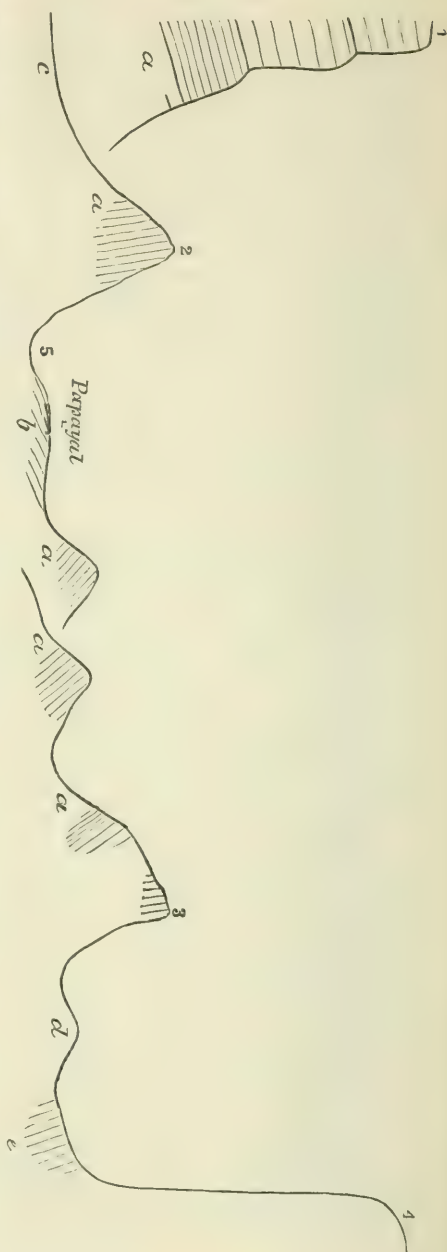
Upon the geological characters of the Sierra Nevada Simons says nothing. The traveller Sivers, who followed him (*Zeitschr. der Gesellsch. für Erdk.*, Berlin, 1888), adheres, as regards geology, to the results obtained by me (p. 57), saying upon the age of this mountain-massif, "It appears, therefore, that the Sierra Nevada de Sta. Marta is a very old piece of the earth's crust which had enjoyed a long continental period when the flooding of its margins by the Cretaceous sea commenced. After these deposits had lasted throughout the

* Steinmann's statement that the Jurassic formation also occurs in New Granada (*Neues Jahrb. der Min. &c.*, 1882) has proved to be erroneous. The Jurassic formation indicated by me, in consequence of Steinmann's publication, in my Map in the "*Géologie*, &c." is consequently to be altered to Cretaceous.

whole Cretaceous period, a folding of them took place in Tertiary times, by which the Sierra de Perija was produced, &c."

The accompanying profile surveyed by me in the district of Papaijal on the river Rancheria (5) (Rio Hacha) and completed near Tomarazon in the west, and passing through the mountains Cerrejon (2) and Potrero de Venancio (3), gives an indication of the stratification of the rocks between the Sierra Nevada (4), and the Cordillera of Ocaña (Perija) which terminates here (1).—*a, a, a*, Red marly sandstone and laminated marl, alternating above with calcareous Cretaceous beds*; *b*, Tertiary strata; *c*, Porphyry with copper ores; *d*, Red quartz-porphry; *e*, Plutonic rocks, such as also form the nucleus of the Sierra Nevada.

* In the uppermost, pale-blue limestone beds of the younger Cretaceous there are, in this district, near Chorrera, towards the summit of the hill, the so-called "Geological organs,"—perpendicular, cylindrical shafts, in parts 10–12 m. high and 4–5 m. in diameter, which I have fully described in the *Zeitschr. d. Geol. Gesellsch.* 1862, and in Westermann's *Monatsheften*, 1863.



XVI. *On Diffraction-Colours, with special reference to Corona and Iridescent Clouds.* By JAMES C. McCONNEL, M.A., Fellow of Clare College, Cambridge.*

[Concluded from vol. xxviii. p. 280.]

3. CORRECTIONS AND ADDITIONS TO THE FIRST PAPER.

IN the article which I wrote two years ago† on this subject occur some actual blunders and some points which require fuller explanation. The most important blunder has been already mentioned‡. In accordance with the usual statement of treatises on Optics, I imagined the central spot of the diffraction diagram to be white, whereas, as a matter of fact, it is coloured with tints similar to those of Newton's first order. Hence what in the calculation I called the first spectrum should really have been called the second; for second spectrum should be written third, and so on. This does not affect the force of the argument against the theory of thin plates, but it makes a considerable difference in the size of the particles deduced from observation. My first inkling of some error in the previous estimate came from the comparison of the sizes of lycopodium seed deduced from measurements of the diffraction-rings round a candle and from actual observation under the microscope. Applying the true theory of observation, it appears that the diameters of the filaments which produce the brightest colours average 0.008 millim. I have measured coronæ produced by filaments varying in diameter between 0.01 and 0.045 millim.

My statement that purple only occurs at the junction of the first two spectra is not strictly correct, for a good purple frequently follows the second red. But the two colours are not likely to be mistaken for each other. The first, in general, inclines much to blue; the second to red. For further description of the colours see the preceding section.

With regard to the distinction between coronæ and iridescences, it is probable that no hard and fast line can be drawn. The optical explanation of the colour is exactly the same, the only difference lying in the character of the cloud. Still, with ice-clouds at any rate, I have never been in doubt in which class to place the colours. In coronæ the rings are complete and perfectly circular, but the tints are in general comparatively poor; whereas in iridescences we have glow-

* Communicated by the Author.

† "On the Cause of Iridescence in Clouds," *Phil. Mag.* Nov. 1887.

‡ See vol. xxviii. pp. 274, 280.

ing colours arranged in scattered patches or, at best, broken rings. It is clear, however, that if the observer could only move close up to one of these patches of glowing colour, a complete system of rings would be developed.

There is a trifling slip in the expression I gave for $\cos \phi'$, in the discussion of reflexion from thin plates. In that formula n should be replaced by $n + \frac{1}{2}$. It will be observed that this change does not affect any part of the argument.

The short paragraph on diffraction-colours seen nearly opposite the sun is founded on a miscalculation, and must be withdrawn. These colours appear to be produced in both water- and ice-clouds. Mr. Omond has sent me a list of several cases in which such glories were seen from Ben Nevis, at temperatures far below the freezing-point*. Their theory seems to be in the most unsatisfactory state. I have come across five different explanations, none of which do I consider satisfactory.

These are the only corrections I have to make, but I find that my description of iridescent clouds has given rise to some misapprehension. Wishing to bring out forcibly the tendency of the colours to arrange themselves symmetrically with regard to the sun, which is one of the main arguments against their being due to thin plates, I used the words: "Within a circle round the sun, radius about 2° , the clouds are white, or faintly tinged with blue. This circular space is surrounded by a ring of yellow, passing into orange." This led some readers to think that these circles were always to be seen; whereas, of course, the yellow is not seen unless there is a cloud of suitable density in a suitable position. The yellow ring is often fairly complete, as every one must have noticed round the moon, but it is very seldom a regular circle like those of coronæ.

The greatest distances from the sun at which I have been able to detect colour, since the date of my first paper, are as follows:—St. Moritz, Oct. 20, 1887, 25° ; Jan. 9, 1888, 34° ; March 10, 29° ; Davos, Dec. 27, 37° . But these extreme colours are only faint pinks and greens. In Colorado iridescences have been observed up to "more than 45° from the sun" ('Nature,' April 21, 1887).

Since I became interested in these colours I have had few opportunities of observing from the sea-level. Still I have seen enough to feel confident—and this view is supported by the testimony of others—that the phenomenon is nearly as

* It is at least possible that in such cases the mists consisted of fine drops of water; and the Ben Nevis observations of fog-bows at all temperatures lend support to this suggestion.

common in England as in the Alps, though fine displays are rare. Common though it be, it has been seen by few. The observer should arm himself with dark spectacles, and, shading his eyes from the direct sunlight with the hand, or preferably with some distant object, such as a building, carefully examine any clouds within 10° of the sun, and he will seldom fail to see colour. A curious illustration of this fact is that iridescences are so frequently seen when the brightness of the sun is reduced by an eclipse, and recorded as remarkable phenomena. To meteorologists these colours should be especially interesting, as manifesting the actual size of the cloud particles*. The following table will be found convenient. To calculate the diameter in millimetres of the average filament in an ice-cloud or of the average drop in a water-cloud, divide the number in the first or second column respectively by the angular distance of the colour from the centre of the sun expressed in degrees.

	Filaments.	Drops.
First yellow	0.022	0.028
„ red	0.028	0.035
„ purple	0.031	0.038
Second blue	0.035	0.042
„ green.....	0.045	0.052
„ yellow	0.051	0.058
„ red	0.057	0.065
„ purple	0.062	0.069
Third green	0.076	0.083
„ red	0.087	0.095
Fourth green	0.106	0.113
„ red	0.124	0.131

A convenient and, in general, sufficiently accurate method of measuring the angle is to find the corresponding length on a pencil held at the full stretch of the two arms. The distance from the eye to the pencil varies only slightly with the position of the body and the altitude of the sun, and can be measured at leisure.

Even when there is no trace of colour we generally see in moderately translucent clouds a great increase of brightness near the sun. With water-drops this might be produced by ordinary refraction, but in frozen clouds it must be attributed

* Fifty years ago Kaemtz used Fraunhofer's results to determine the diameter of the vesicles, as he supposed them to be, of fog (Kaemtz, 'Meteorology,' translated by Walker, p. 111). But the method seems to have been since neglected.

mainly to diffraction, and from the extent of the bright region we can form a rude idea of the size of the particles. The absence of colour will present no difficulty to anyone who has noticed the overpowering brightness of the white central space compared with the surrounding rings of coronæ. It is easy to believe that if there be any considerable variety of size, or if, on the other hand, the majority of particles have any shape other than those approximating to spheres or long cylinders, there will be such blurring of colour that nothing but the bright central white space will survive. As to the size of particle, suppose, for example, the white glow, up to the circle where the brightness is about one fourth of that close by the sun, have a radius of 4° . Taking the number appropriate to the first yellow for filaments and dividing by 4 we obtain 0.0055 mm. We can then assert with some confidence that there are a considerable number of crystals in the cloud at least as thin as 0.005 mm. The estimate is rough, but rough estimates often prove useful. If there is no perceptible increase of brightness in the cloud near the sun we can assert positively that the vast majority of the particles are in no dimension as thin as 0.1 mm.

Unusually vivid iridescences were seen in England and Scotland during the winters 1884-5 and 1885-6, and called forth a number of letters to 'Nature.' The clouds seem to have been of a special type, suspended at a great height in the air, and recognizable even when not coloured *. The bright and varied colours described occurred at distances of over 30° from the sun, so the ice-filaments must have been as fine as 0.001 millim. in diameter. Colours similar, though not so bright, were seen nearly opposite the sun. But the region between 50° and 130° from the sun seems to have been colourless, showing that this was not a case of the action of thin plates.

If cloud-colours are ever formed by thin plates of ice, they may be distinguished by their strong polarization in the plane of the sun. Let us imagine the reflected light to be divided into two parts polarized respectively in and perpendicular to the plane through the sun. Even at 10° from the sun the ratio of these parts is 0.74, at 20° 0.53, at 30° 0.37. In the case of diffracted light the polarization is of the same nature, but not nearly so strong. It probably varies as the square of the cosine of the angle of diffraction. This gives the ratio at 10° 0.97, at 20° 0.88, at 30° 0.75. Thus at 10° the polariza-

* See especially letters by Mr. T. W. Backhouse, Feb. 19, 1885, and Mar. 25, 1886. One cloud, from simultaneous observations at different places, was found to be at least 11 miles high.

tion of diffraction-colours could not be detected with a nicol prism, though readily seen in thin-plate colours. At 20° the variation of brightness, as the nicol is rotated, should in one case be in the ratio 4:1, in the other 4:3; at 30° , 7:1 and 7:4 respectively. As I have pointed out before, thin-plate colours are most likely to be seen at 20° or 30° from the sun.

I have recently looked up Fraunhofer's own account of his observations on the light diffracted by a slit*. I find that, though in his formulated statement he says that the deviations of the red bands are in the ratio 1 : 2 : 3 . . . , yet what he actually measured were the boundaries between successive spectra. He describes the first spectrum as ending with red, and the second as commencing with indigo, blue, &c., and remarks that each spectrum fades by insensible degrees into the next. He measured the extreme limits of the first four spectra, and found they corresponded to "retardations" of 0.0000211 Paris inch or 0.000057 centim. multiplied respectively by 1, 2, 3, 4. By referring to the continuous curve in my diagram, it will be seen that the first three of these points lie nearly on the line from W to the violet corner, while the fourth would lie nearly in that line produced. Thus he evidently included what I have called purple in the red.

4. BISHOP'S RING †.

One of the most interesting examples of a diffraction-corona was the great ring round the sun produced by Krakatoa dust. In the report of the Krakatoa Committee of the Royal Society there is a section devoted to this subject, in which two serious blunders occur, and some important considerations are omitted. So a few remarks on the subject may not be out of place.

The corona is generally described as "a whitish silvery patch surrounded by a brownish fringe," or in similar terms‡. Prof. Cornu studied the colours carefully and says that in favourable circumstances the order was, "Proceeding from the centre outwardly, clear azure blue, neutral grey, brown-

* Schumacher's *Astronomische Abhandlungen*, vol. ii. 1823.

† Since this section was written I have received from Dr. J. Pernter a copy of his paper "Zur Theorie des Bishop'schen Ringes" (*Meteorologische Zeitschrift*, Nov. 1889), in which some of my remarks are anticipated. Pernter deduces the size of the particles from Fraunhofer's measurements of the diffraction pattern of a circular aperture, and obtains results not very different from mine. In this case also Fraunhofer measured the boundaries of the spectra and included my purple in the red.

‡ Krakatoa Report, p. 233.

yellow, orange-yellow, coppery red, purple-red, and dull violet, which is analogous to the succession of the colours of the first ring of diffraction-coronæ presented by thin clouds"*. This evidence will probably be considered conclusive.

Some observers thought the red ring had some connexion with an ice halo, as it happened to have about the same radius; and it may be remarked that, when the ice prisms are small, diffraction must greatly modify the appearance of a halo. The narrow beam of light, which passes through the two faces of a hexagonal prism in the position of minimum deviation, must behave as if it had passed through a narrow slit in an opaque screen. Thus I find that a beam of red light which traversed a prism of 0.03 millim. greatest diameter would be spread out by diffraction to an angular breadth of 5° , and other colours less in proportion to their wave-lengths. This spreading out would probably be fatal to such an indistinct phenomenon as an ordinary halo. Still, if the mass of prisms were of great depth, the halo might survive with an aspect very different to its usual one. One thing that enables us to say with certainty that Bishop's ring was a corona and not a halo, is that, however a halo be modified, the brightness outside the red ring will be greater than that inside, while in a corona the reverse holds good, and Bishop's ring was the outer border of a bright space.

Mr. Douglas Archibald, from a consideration of all the observations, selects the following radii: for the inner border of the red ring $10^\circ 30'$, for the middle $15^\circ 10'$, for the outer border $22^\circ 45'$. Taking $15^\circ 10'$ and applying the figure given in the table above for the first red with spheres, we find the average diameter of the particles to be 0.0023 millim. The ring was evidently broadened out by the irregular diameters of the particles. Assigning the outer border of the ring to the first purple and using the radius $22^\circ 45'$, we find for the diameter of the particles 0.00167 millim., and we can assert that there were a considerable number as small as this. It does not follow that smaller sizes were not well represented. The brightness of the diffracted light is proportional to the fourth power of the diameter of the particle, so the smaller sizes are severely handicapped. With regard to the upper limit of size, we may perhaps take the first yellow as the inner border of the brownish or reddish ring, which gives 0.0027 millim. By using the value for the red, we find that there were certainly not many particles broader than 0.0033 millim.

Mr. Douglas Archibald † used the formula $\sin(\text{radius}) = N\lambda/d$, where d is the diameter of the particle and N a constant.

* *L. c.* p. 252.

† *L. c.* p. 257.

It is apparent from the context that he intends to use the value of N which gives the first bright ring in homogeneous light. This is the very mistake into which I myself fell. But there is another mistake. Through some oversight the value of N , with which he was supplied by Prof. Stokes, is 0.7655, which applies to the first *dark* ring when the diffracting aperture itself is a narrow ring of diameter d^* . When the diffracting aperture is circular or, what comes to the same thing, the diffracting obstacle is spherical, the value of N for the first bright ring is 1.64. It happens that the two errors nearly compensate each other; so that he obtains $d=0.00162$ millim.

If the diffracting particles had been very thin circular disks floating with their planes horizontal, the ring would only have been circular when the sun was in the zenith. When the sun was at an altitude of 30° , the vertical angular diameter of the ring would have been about twice as great as the horizontal. Nothing like this was observed, so we must suppose the particles to have been either nearly spherical or else lying with their planes in all positions at random. A small dilatation of the ring was observed about sunset, especially of the vertical radius, amounting to 3° and 6° at zenith distances of the sun 85° and 90° ; but it is difficult to conceive any shape or orientation of the particles which would explain this.

As the sun gets low the higher regions of the air become relatively brighter, so that if these contain smaller particles the radius of the ring will increase. On the other hand, as the red rays become relatively more powerful, the red ring will become brighter and broaden out towards the sun. This seems to agree with what was observed.

Hotel Buol, Davos,
November 30, 1889.

XVII. *On the Vibrations of an Atmosphere.*

By Lord RAYLEIGH, *Sec. R.S.*†

IN order to introduce greater precision into our ideas respecting the behaviour of the Earth's Atmosphere, it seems advisable to solve any problems that may present themselves, even though the search for simplicity may lead us to stray rather far from the actual question. It is proposed here to consider the case of an atmosphere composed of gas which

* *Encyc. Brit.*, Wave Theory, p. 432.

† Communicated by the Author.

obeys Boyle's law, viz. such that the pressure is always proportional to the density. And in the first instance we shall neglect the curvature and rotation of the earth, supposing that the strata of equal density are parallel planes perpendicular to the direction in which gravity acts.

If p , σ be the equilibrium pressure and density at the height z , then

$$\frac{dp}{dz} = -\sigma g; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and by Boyle's law,

$$p = a^2 \sigma, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a is the velocity of sound. Hence

$$\frac{d\sigma}{\sigma dz} = -\frac{g}{a^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\sigma = \sigma_0 e^{-gz/a^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where σ_0 is the density at $z=0$. According to this law, as is well known, there is no limit to the height of the atmosphere.

Before proceeding further, let us pause for a moment to consider how the density at various heights would be affected by a small change of temperature, altering a to a' , the whole quantity of air and therefore the pressure p_0 at the surface remaining unchanged. If the dashes relate to the second state of things, we have

$$\sigma = \sigma_0 e^{-gz/a^2}, \quad \sigma' = \sigma'_0 e^{-gz/a'^2},$$

$$p = p_0 e^{-gz/a^2}, \quad p' = p'_0 e^{-gz/a'^2},$$

while

$$a^2 \sigma_0 = a'^2 \sigma'_0.$$

If $a'^2 - a^2 = \delta a^2$, we may write approximately

$$\frac{p' - p}{p_0} = \frac{\delta a^2}{a^2} \frac{gz}{a^2} e^{-gz/a^2}.$$

The alteration of pressure vanishes when $z=0$, and also when $z=\infty$. The maximum occurs when $gz/a^2=1$, that is when $p=p_0/e$. But relatively to σ , $(p'-p_0)$ increases continually with z .

Again, if ρ denote the proportional variation of density,

$$\rho = \frac{\sigma' - \sigma}{\sigma} = \frac{a^2}{a'^2} (e^{-gz/a'^2 + gz/a^2} - 1).$$

If $a'^2 > a^2$, ρ is negative when $z=0$, and becomes $+\infty$ when $z=\infty$. The transition $\rho=0$ occurs when $gz/a^2=1$, that is at the same place where $p'-p$ reaches a maximum.

In considering the small vibrations, the component velocities at any point are denoted by u, v, w , the original density σ becomes $(\sigma + \sigma\rho)$, and the increment of pressure is δp . On neglecting the squares of small quantities the equation of continuity is

$$\sigma \frac{d\rho}{dt} + \sigma \frac{du}{dx} + \sigma \frac{dv}{dy} + \sigma \frac{dw}{dz} + w \frac{d\sigma}{dz} = 0;$$

or by (3),

$$\frac{d\rho}{dt} + \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} - \frac{gw}{a^2} = 0. \quad . \quad . \quad (5)$$

The dynamical equations are

$$\frac{d\delta p}{dx} = -\sigma \frac{du}{dt}, \quad \frac{d\delta p}{dy} = -\sigma \frac{dv}{dt}, \quad \frac{d\delta p}{dz} = -g\sigma\rho - \sigma \frac{dw}{dt};$$

or by (3), since

$$\delta p = a^2 \sigma \rho,$$

$$a^2 \frac{d\rho}{dx} = -\frac{du}{dt}, \quad a^2 \frac{d\rho}{dy} = -\frac{dv}{dt}, \quad a^2 \frac{d\rho}{dz} = -\frac{dw}{dt}. \quad . \quad . \quad (6)$$

We will consider first the case of one dimension, where u, v vanish, while ρ, w are functions of z and t only. From (5) and (6),

$$\frac{d\rho}{dt} + \frac{dw}{dz} - \frac{gw}{a^2} = 0, \quad . \quad . \quad . \quad (7)$$

$$a^2 \frac{d\rho}{dz} = -\frac{dw}{dt}; \quad . \quad . \quad . \quad (8)$$

or by elimination of ρ ,

$$\frac{1}{a^2} \frac{d^2 w}{dt^2} = \frac{d^2 w}{dz^2} - \frac{g}{a^2} \frac{dw}{dz}. \quad . \quad . \quad . \quad (9)$$

The right-hand member of (9) may be written

$$\left(\frac{d}{dz} - \frac{g}{2a^2} \right)^2 w - \frac{g^2}{4a^4} w,$$

and in this the latter term may be neglected when the variation of w with respect to z is not too slow. If λ be of the nature of the wave-length, dw/dz is comparable with w/λ ; and the simplification is justifiable when a^2 is large in comparison with $g\lambda$, that is when the velocity of sound is great in comparison with that of gravity-waves (as upon water) of wave-length λ . The equation then becomes

$$\frac{d^2 w}{dt^2} = a^2 \left(\frac{d}{dz} - \frac{g}{2a^2} \right)^2 w;$$

or, if

$$w = W e^{\frac{1}{2}gz/a^2}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\frac{d^2 W}{dz^2} = a^2 \frac{d^2 W}{dz^2}; \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the ordinary equation of sound in a uniform medium. Waves of the kind contemplated are therefore propagated without change of type except for the effect of the exponential factor in (10), indicating the increase of motion as the waves pass upwards. This increase is necessary in order that the same amount of energy may be conveyed in spite of the growing attenuation of the medium. In fact $w^2 \sigma$ must retain its value, as the waves pass on.

If w vary as e^{int} , the original equation (9) becomes

$$\frac{d^2 w}{dz^2} - \frac{g}{a^2} \frac{dw}{dz} + \frac{n^2 w}{a^2} = 0. \quad . \quad . \quad . \quad . \quad (12)$$

Let m_1, m_2 be the roots of

$$m^2 - \frac{g}{a^2} m + \frac{n^2}{a^2} = 0,$$

so that

$$m = \frac{g \pm \sqrt{(g^2 - 4n^2 a^2)}}{2a^2}, \quad . \quad . \quad . \quad . \quad (13)$$

then the solution of (12) is

$$w = A e^{m_1 z} + B e^{m_2 z}, \quad . \quad . \quad . \quad . \quad (14)$$

A and B denoting arbitrary constants in which the factor e^{int} may be supposed to be included.

The case already considered corresponds to the neglect of g^2 in the radical of (13), so that

$$m = \frac{g \pm 2nai}{2a^2},$$

and

$$w e^{-\frac{1}{2}gz/a^2} = A e^{in(t+z/a)} + B e^{in(t-z/a)}. \quad . \quad . \quad . \quad (15)$$

A wave propagated upwards is thus

$$w = e^{\frac{1}{2}gz/a^2} \cos n(t - z/a), \quad . \quad . \quad . \quad . \quad (16)$$

and there is nothing of the nature of reflexion from the upper atmosphere.

A stationary wave would be of type

$$w = e^{\frac{1}{2}gz/a^2} \cos nt \sin \frac{nz}{a}, \quad . \quad . \quad . \quad . \quad (17)$$

w being supposed to vanish with z . According to (17), the

energy of the vibration is the same in every wave-length, not diminishing with elevation. The viscosity of the rarefied air in the upper regions would suffice to put a stop to such a motion, which cannot therefore be taken to represent anything that could actually happen.

When $2na < g$, the values of m from (13) are real, and are both positive. We will suppose that m_1 is greater than m_2 . If w vanish with z , we have from (14) as the expression of the stationary vibration

$$w = \cos nt(e^{m_1 z} - e^{m_2 z}), \quad . \quad . \quad . \quad . \quad (18)$$

which shows that w is of one sign throughout. Again by (8)

$$a^2 \rho = n \sin nt \left\{ \frac{e^{m_1 z}}{m_1} - \frac{e^{m_2 z}}{m_2} \right\}. \quad . \quad . \quad . \quad . \quad (19)$$

Hence $d\rho/dz$, proportional to w , is of one sign throughout; ρ itself is negative for small values of z , and positive for large values, vanishing once when

$$e^{(m_1 - m_2)z} = m_1/m_2. \quad . \quad . \quad . \quad . \quad (20)$$

When n is small, we have approximately

$$m_1 = \frac{g}{a^2} - \frac{n^2}{g}, \quad m_2 = \frac{n^2}{g}, \quad . \quad . \quad . \quad . \quad (21)$$

so that ρ vanishes when

$$e^{gz/a^2} = \frac{g^2}{n^2 a^2}, \quad . \quad . \quad . \quad . \quad (22)$$

or by (4) when

$$\sigma/\sigma_0 = n^2 a^2 / g^2. \quad . \quad . \quad . \quad . \quad (23)$$

Below the point determined by (23) the variation of density is of one sign and above it of the contrary sign. The integrated variation of density, represented by $\int_0^\infty \sigma \rho dz$, vanishes, as of course it should do.

It may be of interest to give a numerical example of (23). Let us suppose that the period is one hour, so that in C.G.S. measure $n = 2\pi/3600$. We take $a = 33 \times 10^4$, $g = 981$. Then

$$\sigma/\sigma_0 = \frac{1}{290};$$

showing that even for this moderate period the change of sign does not occur until a high degree of rarefaction is reached.

In discarding the restriction to one dimension, we may suppose, without real loss of generality, that $v=0$, and that u, w, ρ are functions of x and z only. Further, we may suppose that x occurs only in the factor e^{ikx} ; that is, that the motion is periodical with respect to x in the wave-length $2\pi/k$; and that as before t occurs only in the factor e^{int} . Equations (5), (6) then become

$$in\rho + iku + \frac{dw}{dz} - \frac{gw}{a^2} = 0, \quad . \quad . \quad . \quad (24)$$

$$a^2 k \rho = -nu, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$a^2 d\rho/dz = -i n w; \quad . \quad . \quad . \quad . \quad . \quad (26)$$

from which if we eliminate u, w , we get

$$\frac{d^2 \rho}{dz^2} - \frac{g}{a^2} \frac{d\rho}{dz} + \left(\frac{n^2}{a^2} - k^2 \right) \rho = 0, \quad . \quad . \quad . \quad (27)$$

an equation which may be solved in the same form as (12).

One obvious solution of (27) is of importance. If $d\rho/dz=0$, so that $w=0$, the equations are satisfied by

$$n^2 = k^2 a^2. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Every horizontal stratum moves alike, and the *proportional* variation of density (ρ) is the same at all levels. The possibility of such a motion is evident beforehand, since on account of the assumption of Boyle's law the velocity of sound is the same throughout.

In the application to meteorology, the shortness of the more important periods of the vertical motion suggests that an "equilibrium theory" of this motion may be adequate. For vibrations like those of (28) there is no difficulty in taking account of the earth's curvature. For the motion is that of a simple spherical sheet of air, considered in my book upon the 'Theory of Sound,' § 333. If r be the radius of the earth, the equation determining the frequency of the vibration corresponding to the harmonic of order h is

$$n^2 r^2 = h(h+1)a^2, \quad . \quad . \quad . \quad . \quad (29)$$

the actual frequency being $n/2\pi$. If τ be the period, we have

$$\tau = \frac{2\pi r}{a \sqrt{h(h+1)}}. \quad . \quad . \quad . \quad . \quad (30)$$

For $h=1$, corresponding to a swaying of the atmosphere

from one side of the earth to the opposite,

$$\tau_1 = \frac{2\pi r}{a\sqrt{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

and in like manner for $h=2$,

$$\tau_2 = \frac{2\pi r}{\sqrt{6}} = \frac{\tau_1}{\sqrt{3}}. \quad . \quad . \quad . \quad . \quad (32)$$

To reduce these results to numbers we may take for the earth's quadrant

$$\frac{1}{2}\pi r = 10^6 \text{ cm.};$$

and if we take for a the velocity of sound at 0° as ordinarily observed, or as calculated upon Laplace's theory, viz. 33×10^3 cm./sec., we shall find

$$\tau_1 = \frac{4 \times 10^9}{\sqrt{2 \times 33 \times 10^3}} \text{ seconds} = 23.8 \text{ hours.}$$

On the same basis,

$$\tau_0 = 13.7 \text{ hours.}$$

It must, however, be remarked that the suitability of this value of a is very doubtful, and that the suppositions of the present paper are inconsistent with the use of Laplace's correction to Newton's theory of sound propagation. In a more elaborate treatment a difficult question would present itself as to whether the heat and cold developed during atmospheric vibrations could be supposed to remain undissipated. It is evidently one thing to make this supposition for sonorous vibrations, and another for vibrations of about 24 hours period. If the dissipation were neither very rapid nor very slow in comparison with diurnal changes—and the latter alternative at least seems improbable—the vibrations would be subject to the damping action discussed by Stokes*.

In any case the near approach of τ_1 to 24 hours, and of τ_2 to 12 hours, may well be very important. Beforehand the diurnal variation of the barometer would have been expected to be much more conspicuous than the semi-diurnal. The relative magnitude of the latter, as observed at most parts of the earth's surface, is still a mystery, all the attempted explanations being illusory. It is difficult to see how the operative forces can be mainly semi-diurnal in character; and if the effect is so, the readiest explanation would be in a near coincidence between the natural period and 12 hours. According to this view the semi-diurnal barometric move-

* Phil. Mag. [4] i. p. 305, 1851. 'Theory of Sound,' § 247.

ment should be the same at the sea-level all round the earth, varying (at the equinoxes) merely as the square of the cosine of the latitude, except in consequence of local disturbances due to want of uniformity in the condition of the earth's surface.

Terling Place, Witham,
Dec. 1889.

XVIII. *Process of Plotting Curves by the Aid of Photography.*
By ERIC GERARD, *Professor of Electricity at Montefiore University, Liège*.*

METHODS of registering automatically are being employed more and more in the "technique" of natural sciences. The indicator serves as a faithful and patient observer when it has to register phenomena of slow movement. It is also possible to make use of it to note displacements which are too rapid for our senses to observe. The registering of rapid movements is most often effected by a style fastened to a movable arm, which traces on a rotating cylinder covered with lampblack. When the movement of the cylinder is not perfectly regular, and when the law of displacement in terms of its duration is required, the time is registered by the aid of an electric chronograph regulated by a tuning-fork. This process has led to important results; but it is not easily applied when it is required to mark the path described by very light moving arms, or indicators, with very small forces to move them. In such cases the optical method by mirror-galvanometer, with lamp; and with the traces fixed by means of photography, is available. This has been done for curves measuring variable electric currents, which have been the subject of research in the laboratory of the Montefiore Electro-technical Institute in the University of Liège.

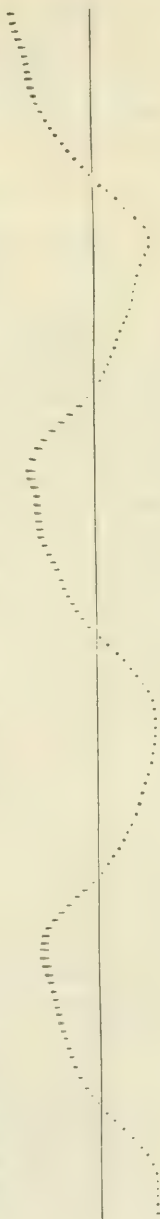
For this purpose we require an extremely delicate deadbeat galvanometer, with a movable coil of little inertia (electromagnetic system of MM. Despretz and D'Arsonval). A beam from an electric lamp was thrown upon a small concave mirror fixed to the movable part of the galvanometer, so as to give an image, focused by a lens upon a registering cylinder, which was covered beforehand with a sheet of paper sensitized with a gelatine emulsion of bromide of silver. The time was recorded simultaneously on the cylinder by means of a second beam of light thrown on a movable concave mirror, the axis of which was placed on the prong of an electric tuning-fork.

* Communicated by Sir W. Thomson.

A simplification of this method by which the need for the separate *time-curve* is done away with has been worked out successfully and has given us good results, in the Montefiore Institute. The photographic record is produced by a spark obtained from a Ruhmkorff coil of ordinary dimensions. The induction-spark passes between a strip of magnesium and a carbon-point, like that which is used in an arc-lamp. The two electrodes are fixed less than 1 millim. apart. The spark is thrown on a concave mirror attached to a galvanometer-needle, or other body whose motions are to be observed, and reflected thence to the sensitized paper, covering either a rotating cylinder, or a frame descending between guides. The periodicity of the spark determined by the elasticity of a spring used in the inductive break-make, shows naturally the time-interval by divisions on the curve *corresponding to equal accurately known intervals of time*. The breaks are effected by an electric tuning-fork of known period. A single circuit is then formed, including the battery, the primary wire, and the coil of the tuning-fork.

A short white spark is obtained, the position of which is invariable, *by connecting the terminals of the secondary coil to the coatings of a Leyden jar*. Besides, it is well to reduce the image of the spark by introducing a double concave lens in the path of the reflected ray.

By way of illustration of the method we give a curve representing the variation of magnetic field in the air-space of an electromotor. A short length of straight insulated wire was fixed to the armature parallel to the axis. This wire was connected at its end to rings, insulated and fixed on the axle of the motor. Brushes pressing on the rings were connected to a galvanometer, of which a description is given above. The ordinates of the curve



are proportional to the currents induced in the movable wire, and hence represent the intensity of field traversed by the wire in the successive positions which it occupies around its axis. The time-intervals between the ordinates corresponding to the dots forming the curve are hundredths of a second.

XIX. *The Disruptive Discharge of Electricity through Gases.*
By ARTHUR SCHUSTER, F.R.S.*

THE phenomena connected with the disruptive discharge of electricity through gases present some special difficulties which have hitherto withstood all efforts to form a consistent theory. Some time ago † I presented to the Royal Society an outline of a general theory of electric discharge, which has been so favourably received by nearly every one who has been working at the subject ‡ since, that I am encouraged to trace out its consequences in various directions.

Prof. Chrystal § concludes an interesting paper on the disruptive discharge as follows :—

“ With the same end in view, I think it would be desirable to reduce the experiment of Baille and others with spheres, in cases where the surface-density can be calculated, and to examine the values of the dielectric strength in these cases. Until this or something equivalent is done, it is clear that we have really no experimental ground for asserting the existence of such a constant as the dielectric strength of a medium, and therefore cannot take the very first step towards a physical theory of the disruptive discharge, which appears to me to be the next great advance to be made in the science of electricity.”

The present paper is divided into two parts. In the first place I have reduced the numerical results obtained by Baille and Paschen for the discharge between spheres. The result quite justifies Prof. Chrystal's caution, for it appears that the so-called dielectric strength of a medium depends on so many circumstances that there seems to be no sufficient reason to consider it at all as a special property of the medium, except, perhaps, in the case of a perfectly uniform field. In the

* Communicated by the Author.

† Proc. Roy. Soc. xxxvii. p. 317 (1884).

‡ Dessau, Wied. Ann. xxix. p. 362 (1886); Warburg, Wied. Ann. xxxi. p. 545 (1887); Elster and Geitel, Wied. Ann. xxxvii. p. 315 (1889).

§ Proceedings Royal Society Edinburgh, 1881–82, p. 487.

second part of the paper I have discussed the discharge from the theoretical point of view, and although no very definite results are arrived at, owing to our ignorance of the properties of a gas in the layer which is in contact with the solid, I hope the discussion may serve to point out the direction in which further experimentation is at present desirable.

PART I.—*Calculation of the Disruptive Tension at the Surface of a Sphere.*

Whatever idea we may form of the nature of a disruptive discharge, it seems natural to suppose that the spark passes when the normal force at some point of a conductor has reached a certain value. If the discharge takes place between two equal spheres, the point for which the normal force R has to be calculated is on the line joining the centres, where R has its greatest value, for it is there that the spark will pass. I shall use the equations in the form given them by Kirchhoff*; and treat of the case only in which one of the spheres is at potential zero: the problem then consists in finding the potential of the other sphere when the normal force, where it is greatest, has reached a certain value.

If a is the radius of the spheres, ac the distance between the centres, R the normal force at that point of the sphere having a potential V which is nearest to the sphere of zero potential, we have the equation

$$R = Vy/a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where y is a function of c .

Writing

$$2q = c - \sqrt{c^2 - 4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$f(q) = \frac{1}{1-q^2} - \frac{3q}{1-q^6} + \frac{5q^2}{1-q^{10}} - \frac{7q^3}{1-q^{14}} + \dots \pm \frac{mq^{\frac{m-1}{2}}}{1-q^{2m}}, \quad (3)$$

we obtain easily from Kirchhoff's equations,

$$y = \frac{(1+q)^2}{1-q} f(q) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the spheres are near each other so that c is nearly equal to 2, and therefore q is nearly one, the series (3) converges very slowly, and the potential has to be calculated in

* Collected Works, p. 78. There is a misprint in the equation for $d^2U/d\xi^2$ on p. 99. The factor on the right-hand side of the equation should be 4 instead of 3.

some other way ; but the above series will be the most convenient to use whenever the shortest distance between the spheres is greater than the tenth part of the radius of either. The Tables I have prepared will, however, save future observers all trouble of calculation. The following remarks will sufficiently explain the way in which they have been calculated. If, in the general term of series (3), the value of q^{2m} has become sufficiently small to be neglected compared to unity, the remaining terms can be added up without further trouble ; for

$$(m-2)q^{\frac{m+1}{2}} + mq^{\frac{m-1}{2}} = mq^{\frac{m-1}{2}} - (m+2)q^{\frac{m+1}{2}} + (m+4)q^{\frac{m+3}{2}} - \dots$$

When the distance between the spheres is small, it is found more convenient to change the form of series (3) so as to render it more quickly convergent. We may expand each term of the series in powers of q and add up all the first terms, viz. :—

$$1 - 3q + 5q^2 - 7q^3 + \dots = \frac{1-q}{(1+q)^2}.$$

Treating the second and subsequent terms similarly, we obtain

$$f(q) = \frac{(1-q)}{(1+q)^2} + \frac{q^2(1-q^5)}{(1+q^5)^2} + \frac{q^4(1-q^9)}{(1+q^9)^2} + \dots = \frac{q^{2m}(1-q^{4m+1})}{(1+q^{4m+1})^2}.$$

Here, again, the terms may be added up as soon as q^{4m+1} can be neglected. Finally, we may transform the equation still further by multiplying numerator and denominator with $(1-q^{4m+1})^2$, finding thus

$$f(q) = \frac{(1-q)^3}{(1-q^2)^2} + \frac{q^2(1-q^5)^3}{(1-q^{10})^2} + \frac{q^4(1-q^9)^3}{(1-q^{18})^2}.$$

In this equation the denominators very quickly approach the value unity. I have given the series in its various forms as I find that individual computers differ much in their predilections for particular forms, and as the relative trouble of calculating the different series differs according to the degree of accuracy required.

Table I, which I have calculated for the objects of this paper, may be useful to others. The first column gives the distance between the centres in terms of the radius of either sphere, which is the value called c above.

The second, third, and fourth columns give q , $f(q)$, and y , defined by equations (2), (3), and (4). Column 5 gives a quantity, x , which will be found useful for purposes of inter-

polarisation when y is wanted for spheres which are near together and for a value of e not directly given in the Table. If e is the smallest distance between the spheres, that is the explosive distance, x is defined by the equation

$$R = Vx/e. \quad (5)$$

If the normal force were to vary uniformly between the spheres we should have $R' = V/e$, and x is the numerical factor which has to be applied to R' in order to obtain the true value R . Column 5 shows that x varies with sufficient uniformity to render interpolation easy.

TABLE I.

I.	II.	III.	IV.	V.
e .	q .	$f(q)$.	$\frac{(1+q)^2}{1-q} f(q) = y$.	x .
2.1	.7298	.9331	10.335	1.0335
2.2	.6417	.7099	5.342	1.0684
2.3	.5821	.6157	3.687	1.1061
2.4	.5367	.5641	2.875	1.1500
2.5	.5000	.5329	2.398	1.1990
2.6	.4693	.5135	2.089	1.2534
2.7	.4431	.5018	1.876	1.3132
2.8	.4202	.4953	1.723	1.3784
2.9	.4000	.4918	1.607	1.4463
3.0	.3820	.4908	1.517	1.5170
3.5	.3139	.5059	1.273	1.9095
4.0	.2680	.5324	1.169	2.338
5.0	.2087	.5870	1.084	3.252
6.0	.1716	.6338	1.050	4.200
7.0	.1459	.6723	1.034	5.172
8.0	.1270	.7037	1.024	6.144
9.0	.1125	.7299	1.018	7.126
10.0	.1010	.7519	1.014	8.112
100.0	.0400	.8892	1.002	

When the explosive distance becomes less than the tenth part of the radius of the spheres, the series given above cannot be used with advantage. Plana* has written an elaborate memoir on the distribution of electricity on two spheres which are near together. Unfortunately he expresses everything in terms of the total charge of the spheres, which itself is unknown; and his formulæ are not, as far as I can see, useful for our present purpose. Kirchhoff† has given an equation

* *Memorie della reale accademia della scienze di Torino*, tomo vii. 1845.

† *Collected Works*, p. 96.

$$2/(e^{25} + e^{-25}) = 2U = 1 - \frac{2^2 \cdot \zeta^2}{2!} + \frac{5 \cdot 2^4 \cdot \zeta^4}{4!} \\ - \frac{61 \cdot 2^6 \cdot \zeta^6}{6!} + \frac{1385 \cdot 2^8 \cdot \zeta^8}{8!} - \frac{5021 \cdot 2^{10} \cdot \zeta^{10}}{10!}.$$

This series is differentiated with respect to ζ , and the differential coefficients are expressed in terms of $\log q$ by (8). It will not be necessary to give all the steps of the numerical transformations. The result is the series :—

$$\Omega = \frac{1}{2} + A_2(\log q)^2 + A_4(\log q)^4 + A_6(\log q)^6 + \dots \quad (9)$$

where

$$A_2 = \frac{1}{48} = \cdot 02083,$$

$$A_4 = \frac{7}{2304} = \cdot 003038,$$

$$A_6 = \frac{1891}{1935360} = \cdot 000971,$$

$$A_8 = \cdot 000494,$$

$$A_{10} = \cdot 000523.$$

It will be seen that A_{10} is greater than A_8 , and it is impossible to say how large the A coefficients may ultimately become. If we compare together the values of y obtained by means of (6) and the series (7) with those obtained by the series (3), we find that if $\log q$ is so small that all terms higher than the second in the series may be neglected, the agreement is perfect; for larger values of q , although the series seems to converge, it only yields approximate values of y . The convergence of Kirchhoff's series does not necessarily imply the convergence of the series (7), and we must confine ourselves therefore to the use of the latter for such values of $\log q$ only, for which the series can be shown to give correct results with a moderate number of terms. If the explosive distance is small, we may obtain a very simple formula by a further transformation. We call e the explosive distance, and express the normal force in the form Vx/e as in (5). Let x now be expanded in a series proceeding by powers of k where $k^2 = e/a$; a being as before the radius of the sphere. The function of q occurring in the equation (6) is to be expressed in terms of k . Remembering that ca is the distance between the

centres of the spheres, we obtain

$$ca = 2a + e,$$

$$e/a = c - 2 = k^2.$$

Also from (2),

$$c = (1 + q^2)/q = k^2 + 2, \quad . \quad . \quad . \quad . \quad (10)$$

and hence

$$k^2 = (1 - q)^2/q, \text{ or } k = (1 - q)/\sqrt{q}.$$

From (10) it follows that

$$k^2 + 4 = (1 + q)^2/q,$$

and therefore that

$$\frac{(1 + q)^2}{(1 - q)\sqrt{q}} = (k^2 + 4)/k; \quad k\sqrt{k^2 + 4} = \frac{1 - q^2}{q}. \quad (11)$$

Equation (6) now becomes

$$y = -\frac{k^2 + 4}{2k \log q} \Omega,$$

and the series (7), after substitution of $\frac{d_n U}{d\zeta^n}$ in terms of $\log q$, becomes

$$\Omega/\log q = \frac{1}{2 \log q} + \frac{1}{48} \log q + \frac{7}{2304} \log^3 q + \frac{1891}{1935360} \log^5 q + \dots$$

We have still to express $\log q$ in powers of k .

Differentiating (10) we find

$$dq \left(1 - \frac{1}{q^2}\right) = 2k dk,$$

$$\frac{1}{q} \frac{dq}{dk} = \frac{2qk}{q^2 - 1} = -\frac{2}{\sqrt{k^2 + 4}} \text{ from (11);}$$

$$\frac{d \log q}{dk} = -\frac{2}{\sqrt{k^2 + 4}} = -\frac{1}{\sqrt{1 + \frac{k^2}{4}}},$$

$$-\frac{d \log q}{dk} = 1 - \frac{1}{2} \left(\frac{k}{2}\right)^2 + \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{1}{2!} \left(\frac{k}{2}\right)^4 - \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{5}{2} \cdot \frac{1}{3!} \left(\frac{k}{2}\right)^6 + \dots$$

$$-\log q = k - \frac{k^3}{3 \cdot 2^3} + \frac{3}{5 \cdot 2^5 \cdot 2!} k^5 - \frac{3 \cdot 5}{7 \cdot 2^7 \cdot 3!} k^7 + \dots$$

$$= k - \frac{k^3}{24} + \frac{3k^5}{640} - \frac{5}{7168} k^7 + \dots$$

From this series we may obtain $1/\log q$ and any power of $\log q$ in terms of k . Retaining k as far as the fifth power, I find:—

$$-1/\log q = \frac{1}{k} \left[1 + \frac{k^2}{24} - \frac{17}{5760} k^4 - \frac{367}{967680} k^6 \right],$$

$$-(\log q)^3 = k^3 - \frac{k^5}{8},$$

$$-(\log q)^5 = -k^5.$$

Therefore

$$-k\Omega/\log q = \frac{1}{2} + \frac{1}{24} k^2 + \frac{1}{1440} k^4 + \frac{163}{327560} k^6;$$

and hence

$$y = \frac{k^2 + 4}{2k^2} \left[\frac{1}{2} + \frac{k^2}{24} + \dots \right].$$

As $R = Vy'a$ and $e = k^2 a$,

$$R = \frac{V}{e} \left[1 + \frac{1}{3} k^2 + \frac{1}{45} k^4 + \frac{73}{53760} k^6 + \dots \right],$$

and finally,

$$R = \frac{V}{e} \left[1 + \frac{1}{3} \cdot \frac{e}{a} + \frac{1}{45} \frac{e^2}{a^2} + \frac{73}{53760} \frac{e^3}{a^3} + \dots \right]. \quad (12)$$

This series converges rapidly as regards the first few terms if e/a is small, and the results obtained from it may be compared with the values of x given in Table I. Table II. shows the comparison.

TABLE II.

$c-2=e/a.$	x from Series (12).	x from Table I.
·1	1·0335	1·0335
·2	1·0676	1·0684
·5	1·1725	1·1990

The equation (12) gives a result therefore which is too small by 3 per cent. if the distance between the spheres is equal to half their radius; but the result is correct to less than

one part in a thousand if the distance is equal to the fifth part of the radius. This accuracy is quite sufficient in the reduction of any actual observations.

For values of e/a which are smaller than $\cdot 2$ the last term of the series may be neglected, and the equation

$$R = \frac{V}{e} \left[1 + \frac{1}{3} \frac{e}{a} + \frac{1}{45} \frac{e^2}{a^2} \right]$$

may be used; while for distances between the spheres smaller than the tenth part of the radius,

$$R = \frac{V}{e} \left[1 + \frac{1}{3} \frac{e}{a} \right]$$

is correct for all practical requirements. For large distances Table I. must be used.

By the help of this preliminary investigation the reduction of all such observations as Baille's becomes an easy matter. Table III. gives the values of R at which the spark begins to pass according to Baille between spheres of various diameters at different distances. If the so-called dielectric strength is a constant these values should all be equal to each other.

TABLE III.—Values of R for Spark Potential between Spherical Surfaces, in Electrostatic Units.

Explosive distance in centimetres.	Planes.	Radius of Spheres in centimetres.					
		3	1·5	0·5	0·3	0·175	0·05
0·05	179	180	186	190	197	206	292
0·10	147	149	153	163	176	198	376
0·15	135	138	141	157	170	206	425
0·20	127	131	137	154	170	219	460
0·25	122	127	134	154	180	236	478
0·30	118	124	130	156	189	253	494
0·35	116	122	129	159	197	263	516
0·40	113	122	129	164	204	272	528
0·45	112	120	127	166	214	278	540
0·40	112	118	124	157	197	268	539
0·45	110	119	122	167	206	275	578
0·50	109	117	125	166	218	296	608
0·60	106	116	125	181	233	327	639
0·70	106	117	126	188	234	339	667
0·80	106	123	130	192	250	349	685
0·90	105	120	132	191	255	349	708
1·00	106	128	133	194	258	349	733

TABLE IV.—Values of R for Spark Potential between Spherical Surfaces in Electrostatic Units.

Explosive distance in centimetres.	Radius of Spheres in centimetres.		
	1	0·5	0·25
0·01	336	347	372
0·02	258	262	277
0·03	224	236	240
0·04	206	213	222
0·05	194	202	215
0·06	184	190	202
0·07	175	183	193
0·08	172	179	192
0·09	165	174	187
0·10	164	171	187
0·11	160	167	183
0·12	159	167	185
0·14	154	164	187
0·10	166	175	190
0·15	155	165	190
0·20	148	162	198
0·25	145	161	204
0·30	143	163	215
0·35	143	166	226
0·40	142	170	236
0·45	142	174	249
0·50	144	180	256
0·55	145	184	265
0·60	145	190	272
0·70	148	196	281
0·80	151	205	288
0·90	293
1·00	301
1·20	312
1·50	327

In Table IV. Paschen's* recent observations have been similarly reduced. I have taken the values which Paschen gives for the potential necessary to produce the first spark, which, according to him, are slightly larger than those for the subsequent sparks.

Tables III. and IV. will be found to agree with each other in their main features ; and considering the many disturbing influences to which such difficult measurements are subject, the individual numbers also compare well with each other. The main facts which, whatever their causes, can be deduced from the Tables are as follows:—

* Wiedemann's *Annalen*, xxxvii. p. 69 (1889).

(1) For two similar systems of two equal spheres in which only the linear dimensions vary, the breaking-stress is greater the greater the curvature of the spheres.

(2) If the distance between the spheres is increased, the breaking-stress at first diminishes.

(3) There is a certain distance for which the breaking-stress is a minimum.

Let us consider how far all or some of these results may be due to disturbing influences.

I do not think there can be a doubt as to the reality of the influence of curvature, as that influence shows itself persistently at all distances and under all circumstances. Sparks taken between two concentric cylinders show the same effect, as appears from the experiments of Gaugain and Baille. The former*, in a valuable paper, came to the conclusion that when the spark passes, the surface-density is independent of the radius of the outer cylinder. This was to be expected, and shows that Gaugain's method of measuring potential, which does not quite come up to our present standard, was sufficiently accurate for the purpose in view; that is to say, that the indications of his electrometer were really proportional to the potential to be measured. The density σ on the inner cylinder increased, however, with its curvature, and Gaugain found that the relation could be approximately represented by the equation

$$\sigma = \alpha + \beta/\sqrt[3]{r},$$

where, with the units employed by him,

$$\alpha = 2.58 \text{ and } \beta = 25.62.$$

Baille has compared Gaugain's equation with his own experiments, but the values for the surface-density calculated by Baille do not all agree with the numbers deduced by Gaugain himself from the same formula. The cause of the discrepancy is found in the fact that Baille, by an oversight, took r in the above equation to be the radius measured in centimetres, while in the original memoir it stands for the diameter measured in millimetres. I have recalculated Baille's numbers, and the result is given in Table V.

Column v. in that Table shows a decided though not very regular increase of R for diminishing radii of the interior cylinder. This increase comes out more clearly in Gaugain's observations, as he worked with cylinders of much smaller radius. We may use the last column of this Table to reduce, at any rate approximately, Gaugain's numbers to absolute measure. Taking 1.25 as the ratio by means of which Gaugain's numbers are to be divided in order to reduce them to

* *Annales de Chimie et de Physique*, viii. p. 75 (1866).

electrostatic units, we must multiply his surface-density with $4\pi/1.25$, or very nearly with 10, in order to obtain R. The result is given in Table VI., in which r is the radius of the inner cylinder, in centimetres, and R the normal force when a spark begins to pass.

TABLE V.

Values for Spark-potential between Cylinders.

I.	II.	III.	IV.	V.	VI.	VII.
Diameter of internal cylinder. $2r$.	Diameter of external cylinder. $2R$.	Explosive distance.	σ from Baille's observations.	$4\pi\sigma = R$.	σ' from Gaugain's formula.	σ'/σ .
6.28	6.86	.29	7.24	91	9.03	1.25
5.75		.56	8.44	106	9.20	1.09
5.50		.68	8.73	110	9.32	1.07
4.92		.97	9.07	114	9.60	1.06
4.92	5.32	.20	9.07	114	9.60	1.06
4.50		.41	8.33	105	9.72	1.17
4.40		.46	8.25	104	9.84	1.19
4.00		.66	8.59	108	10.07	1.17
3.66		.83	9.92	125	10.30	1.04
4.00	4.45	.23	8.23	103	10.07	1.22
3.66		.40	8.60	108	10.30	1.20
3.10		.68	8.95	112	10.74	1.20
2.49		.98	9.65	121	11.35	1.18
2.49	3.00	.26	8.46	106	11.35	1.34
2.20		.40	8.74	110	11.73	1.34
1.78		.61	9.76	123	12.40	1.27
1.25		.88	10.99	138	13.62	1.24

TABLE VI.

r .	R.
1.5	110
.5	145
.25	168
.05	282
.013	451
.010	491
.006	600

Comparing these numbers with Table II., we find that the disruption-stress is for two coaxial cylinders not very far

different from that found for two spheres placed at such a distance that the disruption-stress is a minimum. Without attaching too great an importance to this apparent coincidence, I think we may safely conclude that the explosive distance is really a function of the curvature of the surface.

The second result which may be deduced from Baille and Paschen's observations is, in my opinion, also well established. The fact that the breaking-stress diminishes for increasing distances between two planes has been known since Sir William Thomson's observations; and it is well brought out in the case of spheres, especially with the larger ones and at small distances, that is, just where the disturbances are smallest. I shall point out in the second part of this paper that the breaking-stress may possibly depend, not only on the state of the field at the point where the spark passes, but in surrounding portions also. The further the spheres are apart, the more nearly will all points of their surface reach the critical density at the same time; and this, in the way to be explained, may help the spark to pass.

I feel much more doubtful as to the reality of the third conclusion, that the explosive stress reaches a minimum with increasing distances and then increases again; but on the whole I believe the evidence to be in its favour.

There are two causes which tend to increase the observed difference of potential when the distance between the spheres is larger. There may in the first place be an appreciable leakage between the electrometer and the electrodes, and the potential registered will in consequence be too high. That leakage actually took place in some of Baille's observations is rendered probable by his observations on cylinders. For a given surface-density on the inner cylinder the state of the medium must be the same whatever the distance of the outer cylinder; and there can be no reason therefore that the breaking-stress will depend on the diameter of that outer cylinder. Gaugain arrived experimentally at the result which was to be expected; but Baille's results, as given in Table V., show a decided tendency towards a larger apparent normal force for greater striking distances, the inner cylinder remaining the same. This seems to me to point to a leakage effect.

The second disturbing cause tending in the same direction is the electrification of the leads. Baille gives us no information as to the disposition of his experiments and the size of the leads, and seems to consider the difference of potential between the electrodes to be the determining cause of the spark and not the rate of fall at their surface. There is no evidence in Baille's paper that he realized the importance of avoiding the presence of electrified surfaces in the neighbour-

hood of his spheres. In the absence of any statement regarding the thickness of leads, we can attach no importance to Baille's results as far as his smallest spheres are concerned. When their diameter is only one millimetre, we may take it for granted that the effect of the wires conveying the charge was considerable.

Paschen has taken this point into consideration, and it follows from the information he gives that with spheres of 5 millimetres in diameter and cylindrical leads of about 3 millimetres diameter the disturbing effect becomes apparent when the sparking distance is greater than 5 millimetres. The leads cannot be reduced in size beyond a certain point with the usual arrangement of the experiments, as the spheres are moved together by a micrometer arrangement, and must of course be kept rigidly in their place.

Making full allowance, however, for the possible effects of leads and leakage, I cannot altogether resist the feeling that the ultimate increase of potential with increasing distance is not altogether due to these causes. My chief reason is the good agreement between Paschen and Baille's results in this respect.

For spheres having a radius of .5 centim. Baille finds the minimum of R to take place when the distance is about half-way between .20 and .25; while Paschen finds the same distance almost exactly the same, though a trifle nearer to .25. It seems difficult to believe that a disturbing cause should affect both observers in exactly the same manner. For the smaller spheres the distance at which the spark potential is a minimum is equal to nearly half the radius of the spheres. This is shown in the following Table:—

TABLE VII.

Radius of spheres.	Explosive distance for smallest normal force.	
	Baille.	Paschen.
centim.		
3	.60	
1.5	.45	
1.042
.5	.22	.25
.3	.17	
.25	11
.175	.10	

PART II.—*Theoretical.*

The attraction between electrified bodies involves a tension along the lines of force in the medium which, with the usual notation, is equal to $KR^2/8\pi$. The specific inductive capacity K of gases is nearly equal to one, and the stress is therefore not much affected by the presence of the gas. It follows that the stress is due to a strain in the interstellar medium, and that the particles of air have nothing to do with it except in so far as we consider them to be conductors which can deflect the lines of force in their neighbourhood. We may imagine the distribution of electricity on each molecule to be regulated by the same law as the distribution on conductors; and in that case the forces tending to produce a passage of electricity between the particles of a gas will be proportional to R^2 , but we do not know how large or how small its value may be. I adopt the theory that the atoms of a molecule carry the same charges as the ions in an electrolyte, and that a spark passes as soon as the forces are sufficient to dissociate the molecules. I take this opportunity to mention that Mr. Giese has in the year 1882, that is, two years previous to the paper in which I first applied this theory to the continuous discharge under reduced pressure, explained by the same hypothesis some of the electric phenomena of flames. The problem of finding the effect of the electric field on the molecules carrying their electric charges is very similar to the problems we meet with in the theory of magnetism. It is usual to consider two vectors inside a magnetized body, the so-called magnetic force H and the magnetic induction B , which are related by the equation

$$B = H + 4\pi I, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where I stands for the intensity of magnetization. In the problems of induced magnetization I is taken to be proportional to the magnetic force defined as the force at the centre of a thin hollow cylinder inside the magnet. It would be more correct to take the magnetizing force as equal to the force at the centre of a space left vacant by the removal of a molecule; and this force could be expressed in terms of the magnetic force as usually defined and the magnetic induction. Let the force within the space left vacant by the removal of one molecule be G ; we may write

$$G = H + nI, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where n is a numerical quantity, which, if the space left vacant

close to the surface of the solid; and if we once admit the possibility of such a contact-layer which diminishes in density by a reduction of pressure, some of the most puzzling facts of the disruptive discharge admit of explanation. One objection, which occurs to me, must be answered. It may be said that if λ is large near the surface of the solid, the spark will start wherever B/λ is largest, and therefore not within the condensed layer, but between it and the remainder of the gas. This objection would be justified if we take the discharge to be a passage of electricity between the molecules; but according to the theory I advocate the dissociation of the molecules may, as already explained, take place more easily in the condensed layer, and probably soonest in direct contact with the metal.

Let us see how far the theory is capable of dealing with the known difficulties of the discharge. I think it will be found sufficient to explain the fact that when the planes or spheres are near together, the normal force sufficient to produce a spark diminishes with increasing distance of the conductors. No explanation which has as yet been suggested can deal with this fact. Prof. Chrystal, in the paper quoted above, has really disposed of all suggestions except one proposed by himself, which, however, does not seem to me to be supported by the observations on spheres. According to the views of this paper the polarized particles within the surface-layer of the gas can slide along the surface of the electrode, and will do so under the action of the electric forces. They will crowd together where the field is strongest, that is to say at that point at which the spark is about to pass. The increased number of particles will increase λ , and will therefore introduce an additional impediment to the formation of the discharge. As the conductors are removed, the field will become more and more uniform all round, the particles will no longer crowd together to the same extent, and the spark will pass more easily.

The increased stress required to produce a spark when the striking-distances are small are due therefore, if I am correct, to the inequality of the field along the surface of the conductor. In the case of plane surfaces which are opposed to each other, the inequality lies between the back and front of the plates, and the surface-particles will be drawn from the back to the front. A fact which seems to me to support the idea that some such thing may take place has been deduced by Mr. G. Jaumann* from a large series of experiments.

* *Wiener Berichte*, July 1888.

Mr. Jaumann comes to the conclusion, which appears well supported by the evidence he gives, that the potential required to produce a spark is the greater the more slowly the potential is raised to its final value. If the potential is raised quickly, so that, according to our view, no time is given for the particles to move along the surface of the conductor, the spark-potential has much smaller values than those usually given.

I am not very confident that a satisfactory explanation of the observed effects of curvature can at present be given. If a surface-layer such as I imagine really exists, forces of the nature of surface-tensions may modify its properties. But it is also possible that the density of the layer may depend, not only on the inequality of the field at different points of the surface, but also on the inequality of the field along the normal to the surface. Particles may be drawn by the electric forces from the gas into the surface-layer whenever there is a rapid variation of the field along the normal. If the polarized particles point in the direction of the lines of force, they will tend to move along them under the action of a force proportional to $\frac{d^2V}{dn^2}$, where V is the potential; and this quantity is the larger for the same value of R the greater the curvature of the surface. It is possible that this is the explanation of the greater spark-potential required for small than for large spheres. The two effects combined may explain the fact that when the spheres are moved away from each other, the breaking-stress at first diminishes and then increases again. For small distances the inequality of the field along the surface causes a crowding of the molecules, and for large distances the inequality of the field along the normal produces the same effect. At intermediate distances it is probable that either a maximum or a minimum of the normal force should take place, but which it should be it is impossible to predict theoretically at present.

I do not attach very much importance to some of the suggestions I have made in order to explain a quantity of very puzzling facts; but it seemed to me to be worth while to place them before the public, as others may be induced to join in an experimental investigation which promises to yield results of importance.

I have to thank Mr. H. Holden for much assistance in the numerical calculations contained in this paper.

XX. *On the Behaviour of Steel under Mechanical Stress.*
 By C. A. CARUS-WILSON, B.A., A.M.I.C.E., Demonstrator
 in the Mechanical Laboratory at the Royal Indian Engineering
 College, Coopers Hill*.

[Plates III.-V.]

THE effect of uniform longitudinal stress on a steel bar is threefold—

- (i.) The molecules are strained.
- (ii.) The elements are strained.
- (iii.) In virtue of the straining of the elements “flow” is produced.

The strain usually observed is the elongation due to flow, which may be recoverable or irrecoverable. The strains of an element can be shown to be a uniform dilatation combined with a uniform shear about an axis parallel to that of the bar; hence the elongation due to flow consists of a sliding combined with an increase of volume.

The state of strain of an element may be conveniently described by defining the shape, size, and orientation of the strain quadric, which is a sphere of radius $3\sqrt{\frac{\bar{k}}{p}}$ combined with an hyperboloid of two sheets whose principal semi-diameter is $\sqrt{\frac{3n}{p}}$ and axis parallel to that of the bar; where p is the intensity of longitudinal stress, n the rigidity, and k the bulk modulus.

Up to a certain stress the elastic properties of the steel are such that the strain produced is recovered when the load is removed, but at that stress the elastic resistance is overcome, and the molecules slide over one another, the strain being permanent.

This sliding beyond the limit of elastic resistance does not continue. The elastic resistance is raised by the sliding, and consequently the sliding is limited.

A stress-strain curve can be drawn which shows the increase of the limit of elastic resistance ρ with sliding; the rate of increase of the former at any point may be measured by observing the angle which the tangent to the curve at that point makes with the axis of strain; I will call this angle ϕ .

The initial value of ρ is often taken as an indication of the “hardness” of the steel, and when ρ is raised by permanent strain the steel is said to be “hardened” thereby. This, however, conflicts with a measure of hardness usually employed,

* Communicated by the Physical Society: read December 6, 1889.

namely the amount of permanent strain caused by performing a given amount of work on a bar.

Thus if a hard steel edge attached to a weight is allowed to fall on the surface of a steel bar, the depth of the indentation is taken as a measure of the softness of the metal.

If we draw the stress-strain curve OP for the steel under examination, the work done in producing a permanent strain OD is the area OPD . If OQ represent the stress-strain curve of a harder bar, the same amount of work, OQC will clearly produce less permanent strain, OC . The hardness then is evidently determined by the form of the curve; but this depends upon the rate of increase of ρ with permanent strain, *i. e.* upon the value of ϕ . Hence $\tan \phi$ is the true measure of the hardness; but $\tan \phi$ is not constant, it diminishes: therefore the initial value of $\tan \phi$ must be taken as the measure of hardness. It will be seen that ρ cannot be taken as a measure of the hardness, for ρ is the same at R and P for the two bars, but the former is obviously the harder*.

We can say, then, that permanent strain raises the limit of elastic resistance, but diminishes the hardness—defined as the rate of increase of ρ with permanent strain.

I imagine it is because the harder steel has the greater value of initial ρ that ρ has been taken as a measure of the hardness.

If a bar of soft steel be taken and cut in four pieces; No. II. "hardened" in oil; No. III. in water [alkaline]; No. IV. in water [acid]; if each piece is now tested we shall obtain stress-strain curves as in fig. 1, Plate III. A curve can be drawn through the points $O A B C D E F$, which I will call the "yield-line"; this will be the locus of all points such as A and F for pieces of the same bar "hardened" to different degrees. The points A, B, C are called the "yield-points."

As the piece is harder the yield-point—or initial limit of elastic resistance—is higher, and the yield AF is less†.

When the yield begins it continues until ρ is raised by a given amount λ . If we could show that λ was the same for each piece, then it would follow that the yields as AF, BE, CD are direct measures of the hardness of the piece.

If there is any inequality or want of homogeneity in the bar due to unequal stresses in the manufacture, there may be one plane or planes along which the limit of elastic resistance is less than along any other.

Hence when this resistance is overcome sliding will take place throughout the bar parallel to that plane or planes until

* If $\tan \phi = 0$, the bar at that point is perfectly plastic.

† Fig. 2, Plate III. is a facsimile of an autographic diagram thus obtained: the steel bar was cut in three pieces; A was soft, B hardened in oil, and C in acid.

the limit of resistance along that plane has been raised, by the sliding, to that of the rest of the bar, when the sliding will henceforth be uniform.

In a bar cut into pieces the required increase is the same in each piece, only in the harder bar less permanent strain is required than in the softer. Hence λ is the same in each piece and the yield is a measure of the hardness.

Steel bars and plates can be shown in which the permanent strain at the yield-point has clearly taken place as a sliding parallel to one plane only.

It would seem that there was an apparent discontinuity in the form of the stress-strain curve at the yield-point.

The question arises whether the curve may not actually be continued through a double inflexion, and be one with the rest of the curve as shown by the dotted lines, fig. 1, Plate III.

Let us imagine a solid model made so as to represent at any point of its surface a particular condition of the bar with respect to stress, strain, and hardness. Let the curves I., II., III., IV. (fig. 1, Plate III.) be placed parallel to one another at distances from the plane $X O Y$ proportional to the hardness which each curve represents, with their origins in the axis $O Z$ (perpendicular to $X O Y$), and let the surface of the model be made to pass evenly through all these curves and other similar curves which would be obtained at higher and lower degrees of hardness.

We see that from the curve which just passes outside the yield-line there is a part of the solid figure entirely wanting. It would seem a much more natural view to suppose that in some sense the successive curves are theoretically continuous, as shown by the dotted line above.

Such a supposition involves a state of affairs in which the limit of elastic resistance decreases as the permanent strain increases.

This would be the case if the sliding at the yield-point instead of taking place simultaneously over the whole bar parallel to one plane only took place as a strain wave passing up or down the bar with a definite velocity without any further increase of load.

This is what actually takes place. Sliding is started at one end and takes place along a definite plane, generally at 45° to the axis; this disturbs the equilibrium of the molecules in the parallel plane next to it, and sliding is induced in this plane, so that a wave of strain passes the whole way up the bar; or sometimes starting from both ends two waves meet in the centre.

The velocity of the wave varies greatly with the quality of the steel; sometimes the wave appears to be instantaneous,

sometimes so slow that it may take 30 seconds to pass up a 10-inch bar, in which case the pencil drawing the stress-strain curve is seen to follow the wave; in the former case the pencil drops as if the bar had broken.

When the wave starts from one end a plane in the centre experiences no permanent sliding until the wave has reached the plane next to it, so that while originally the resistance to sliding was greater than the stress, now it is less; in other words, permanent strain (in an adjacent plane) diminishes the resistance to permanent strain.

The most reliable stress-strain curves are those drawn by Prof. Kennedy's apparatus, and these show a rapid and irregular inflexion at the yield-point (see fig. 3, Plate III.). In these diagrams the record of stress is unaffected by the inertia due to the load.

These stress-strain curves indicate the condition of strain in a steel bar as, by gradually increased stress, the steel is converted from an elastic solid to a viscous fluid. It is interesting to compare such curves for steel of different hardness with the stress-strain curves of a gas at different temperatures (see fig. 4, Plate III.).

We have the effect of increased $\left\{ \begin{array}{l} \text{hardness} \\ \text{temperature} \end{array} \right\}$ doing away with the discontinuity at the $\left\{ \begin{array}{l} \text{yield} \\ \text{boiling} \end{array} \right\}$ line. Also the strong probability that in both cases the apparent discontinuity is really a double inflexion due to a change taking place piecemeal throughout the substance, and inconceivable if the substance be supposed homogeneous (*cf.* Prof. J. Thomson, Proc. Roy. Soc. 1871, no. 130).

[The stress-strain curves shown in the diagram are from Dr. Andrews's paper (Phil. Trans. vol. clix. 1869, p. 575).]

Thus far the strains considered have been those due to relative displacements of the molecules, but it is impossible to conceive that this can take place without the molecules themselves being strained, *i. e.* without a displacement of the atoms.

Such a displacement of atoms, if permanent, would alter the chemical and physical condition of the iron. Hence we must look to the straining of the atoms to account for the change that takes place when a bar is permanently strained, *i. e.* to account for the increase in the value of ρ with permanent strain.

Osmond has proved almost beyond a doubt that the so-called "hardness" of steel is due essentially to the existence of an allotropic modification of iron; that the molecules of iron may be either (α) soft, or (β) hard. (*Cf.* Osmond's '*Études Métallurgiques*,' Paris, Dunod, 1888.)

Hence the change induced in steel by permanent strain must be due to a permanent straining of the atoms in the molecule.

We should then expect to find evidence of a straining of an entirely different order and nature to that due to a molecular disturbance. Such evidence is forthcoming.

It has long been known that if a steel bar lying in a magnetic field of limited intensity be subjected to tension in the direction of the magnetizing force, the magnetization of the bar will be increased.

I have made a series of experiments on this subject, and find that the intensity of magnetization increases regularly with the load up to the yield-point.

The following experiments were made:—

The bar to be tested was turned in the lathe, and a screw cut on each end; it was placed vertically in the testing-machine; to each end was screwed a nut, the top one (A) of gun-metal, the lower one (B) of steel (see fig. 1, Plate IV.). The former was of gun-metal so as to remove the free upper extremity of the bar as far as possible from the neighbourhood of large masses of magnetic material. These nuts rest on steel collars, C C, which have conical surfaces to fit into conical holes in the main shackles, D D, of the testing-machine. The bearing of the nuts on the collars is spherical, so as to allow of a free movement of the specimen, and to ensure a direct pull. A short distance above the upper end of the bar a small magnet, E, is hung by a silk fibre, the suspension of which is rigidly attached to the upper shackle, so that any small motion of the latter involves the same motion of the needle; a silvered mirror is attached to the needle, which reflects a beam of light from a lamp, F, onto a horizontal scale, G; H is a controlling-magnet.

A small displacement is given to the magnet (i.) when there is no load on the bar, and the time of 20 complete oscillations observed; (ii.) the same with a small load on; (iii.) the load is then removed, and the time of 20 oscillations again observed. The results are recorded in the accompanying Table.

Experiment I.—Bar of soft steel, never loaded before: cross sectional area 0·306 square inch, 19·5 inches long; elongations measured on $10''$ by a vernier and microscope reading to thousandths of an inch.

An automatic stress-strain diagram was taken (see curve A, Plate IV.). The time of 20 oscillations of the needle was first observed with the bar out—102·6 seconds. From this was deduced x^2 , the square of the number of oscillations per minute, and this was deducted from N^2 , the same when the bar

was in place. The results are plotted on fig. 1, Plate V. as two curves, the upper one, A_1 , being the curve of temporarily-induced magnetism, with load on, and the lower one, A_2 , that of permanent magnetism, with load off. The arrow shows the yield-point. The two curves cross one another twice, and coincide in a third point. The third curve, A_3 , is the curve of extensions from the second column of the Table, 186 times full size. Curve A_4 is the curve of permanent set, same scale as A_3 . This bar was broken. The last observation was after the fracture.

Experiment II.—Bar of soft steel never loaded before : cross-sectional area 0.308 square inch, 19 inches long; diagram measures elongations of $10''$; square of number of oscillations per minute with bar out 121; ditto, bar in, no load on, 1849. The results are plotted as a curve in fig. 2, Plate V. The arrow shows the yield-point. The observations at this point were taken after the set. The stress-strain diagram is shown at B, Plate IV. This bar was broken.

Experiment III.—Wrought-iron bar never loaded before : cross-sectional area 0.203 square inch. The extensions on the diagram, C, Plate IV., are on a length of six inches. The results are recorded in the Table, and plotted on fig. 5, Plate III., the ordinates here representing simply the square of the number of oscillations per minute. The arrow shows the yield-point. The curves intersect twice. This bar was not broken.

The circles show the loads at which observations were made.

From the curves on Plates III. and V., it is evident that the magnetic induction is increased in a regular way by increased stress, and that the effect is largely permanent; a point is reached, before the yield-point, where the effect produced is wholly permanent. The two curves continue side by side up to the yield-point, when the large permanent set which then takes place completely upsets the former condition of the bar, as might have been expected. The temporary effect is roughly proportional to the elastic extension below the yield-point.

The conclusions to which I am drawn by these experiments are :—

(i.) Mechanical straining produces an “atomic disturbance” in a bar which increases regularly with the stress.

(ii.) For small stresses the disturbance is only partly permanent, but as the yield-point is neared it becomes wholly permanent.

(iii.) The magnetic properties of a loaded bar are in general different from those of the same bar unloaded, but there is a certain stress or range of stresses over which the bar has the same magnetic properties whether the load be on or off.

In Experiment I. the range of stress referred to in (iii.) is about 15 to 22 tons per square inch, the latter being the yield-point; and in Experiment III. it is about 10 to 15 tons per square inch, the latter being the yield-point. In Experiment II. the critical stress appears to coincide very nearly with the stress at the yield-point.

It is interesting to compare these results with those obtained by Joule. In his 'Scientific Papers,' pp. 253-256, Joule shows that an iron or steel bar elongates on being magnetized, but that if the bar is strained, the effect is reduced until, at a certain load, no effect is observed, and if the load be further increased, magnetization produces a shortening of the bar. These experiments were made with soft iron and steel wires.

Joule's experiments show that magnetization produces a minute elongation of a bar, those quoted above show that mechanical stress increases the magnetization of a bar, *i. e.* mechanical stress produces a change similar to that produced by magnetization. It would seem, then, that Joule's critical point of no elongation (+ or -) must be reached when the molecular elongation produced by the mechanical stress is the same as that which would be produced independently by a certain given intensity of magnetization. For at that point, the molecular elongation having already been produced by mechanical stress, the effect of the given magnetization would be nil, *i. e.* there would be no further elongation (+ or -). Now, taking an intensity of magnetization, denoted by 5 in Joule's experiments, we see that this produces an elongation in a 12 inch length of soft iron wire (0.25 in. diam.) of $\frac{4}{150,960}$ in.; assuming Young's modulus for the iron at 13×10^3 tons per square inch, the mechanical stress required to produce this elongation would be about 0.03 ton per square inch.

According to Joule's experiments the critical stress is at about 6 tons per square inch, *i. e.* in order to produce this molecular elongation by mechanical means we require an elongation of the bar 200 times as great as that which accompanies the same effect produced by magnetization.

We are thus dealing with two distinct kinds of elongations—firstly, that produced by a relative motion of the molecules; and secondly, that produced by a straining of the molecules themselves.

It is clear that if the atomic displacement should be permanent, there would be a permanent change in the physical and chemical properties of the iron; and as there certainly is a change produced by permanent set, it is highly probable that we must look to such a straining of the molecule to account for it.

Thus, taken in conjunction with Osmond's experiments, those quoted above would seem to show that the increase in the value of the limit of elastic resistance with permanent strain is due to a permanent straining of the individual molecules.

Experiment I.—Steel Bar.

Load.	Micrometer.	Time in seconds of 20 vibrations.	$\frac{N^2 - \sigma^2}{10}$.	Load.	Micrometer.	Time in seconds of 20 vibrations.	$\frac{N^2 - \sigma^2}{10}$.
0.0	1.417	24.9	218	0.0	1.418	18.9	389
0.1	1.417	24.85	219	5.4	1.457	18.7	398
0.2	1.417	25.0	217	0.0	1.418	18.7	398
0.4	1.418	24.8	221	0.0	1.418	18.65	400†
0.0	1.417	24.85	219	5.6	1.458	18.65	400
0.6	1.420	24.75	221	0.0	1.418	18.6	403
0.8	1.420	24.6	224	5.8	1.463	18.7	398
1.0	1.422	24.55	225	0.0	1.420	18.5	407
0.0	1.417	24.9	219	6.0	1.465	18.3	416
1.2	1.424	24.1	234	0.0	1.420	18.5	407
1.4	1.425	23.7	243	6.2	1.465	18.35	414
1.6	1.426	23.35	250	0.0	1.420	18.4	412
1.8	1.427	22.4	273	6.4	1.467	18.2	421
2.0	1.428	21.8	289	0.0	1.421	18.55	405
0.0	1.417	22.6	268	6.6	1.469	18.3	416
0.0	1.417	22.5	271*	0.0	1.421	18.3	416
2.2	1.430	20.9	316	6.8	1.470	18.0	431
2.4	1.431	20.55	327	0.0	1.421	18.6	403
2.6	1.433	20.4	332	7.0 §			
2.8	1.434	20.3	336	0.0	1.455	18.8	394
3.0	1.436	19.85	352	7.0 §			
0.0	1.417	20.7	322	0.0	1.507	19.2	377
0.0	1.417	20.75	321*	7.0 §			
3.2	1.437	19.6	361	0.0	1.538	19.4	369
3.4	1.438	19.5	365	0.0	1.538	19.5	365†
3.6	1.439	19.65	359	7.7	2.095	17.95	433
3.8	1.440	19.6	361	0.0	2.036	25.35	210
4.0	1.442	19.45	367	8.0	2.178	16.5	515
0.0	1.417	20.05	344	0.0	2.112	25.05	216
0.0	1.417	19.9	350*	8.3	2.323	16.8	497
4.2	1.444	19.1	381	0.0	2.248	25.45	209
0.0	1.417	19.75	355	8.6	2.455	16.65	506
4.4	1.446	19.15	379	0.0	2.374	25.7	204
0.0	1.417	19.45	367	9.0	2.692	17.05	482
4.6	1.451	19.1	381	0.0	2.616	26.4	193
0.0	1.418	19.5	365	9.3	2.981	16.8	497
4.8	1.452	18.8	394	0.0	2.893	26.35	194
0.0	1.418	18.9	389	10.0	17.4	462
0.0	1.418	18.9	389†	0.0	27.5	177
5.0	1.453	18.85	391	10.5	17.35	465
0.0	1.418	19.05	383	0.0	28.0	170
5.2	1.455	18.65	400	10.87	18.1	426

* After 10".

† After 5".

‡ After 17 hours.

§ Load removed after small permanent set.

|| After fracture.

Experiment III.—Wrought-iron Bar.

Load in tons.	<i>n</i> . Time in seconds of 20 vibrations.	$n^{-2} \cdot 10^5$.	Load in tons.	<i>n</i> . Time in seconds of 20 vibrations.	$n^{-2} \cdot 10^5$.
0.0	17.25	336	0.0	13.2	574
0.5	16.8	354	2.7	13.25	570
0.0	17.1	342	0.0	12.85	606
0.0	16.9	350 *	3.0	13.0	592
0.7	15.25	430	0.0	13.3	565
1.0	14.05	507	3.12	12.75	615†
0.0	14.7	463	0.0	14.85	453
1.3	13.05	587	3.4	12.75	615
1.6	13.15	578	0.0	15.2	433
0.0	13.5	549	3.8	12.85	606
2.0	12.95	596	4.2	13.55	545
0.0	12.95	596	0.0	16.25	379
2.2	13.1	583	4.4	13.55	545
0.0	13.4	557	0.0	15.95	393
2.4	12.8	610			

* After one hour.

† After the permanent set.

XXI. *On Sensitive Galvanometers.*

By Prof. A. GRAY, M.A.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

I HAVE read with interest and also some surprise the remarks made by Prof. Threlfall in his paper in the Phil. Mag. for December last on the galvanometer invented by my brother and myself, and described by us in the 'Proceedings of the Royal Society,' for 1884 (vol. xxxvi.). The notes of our original observations on the sensitiveness of that instrument are I believe in the possession of my brother, who is now in the United States, and are at present therefore beyond my reach. I have, however, set up the instrument, and am now able to state some results I have obtained with it in its present state. The sensitiveness I have attained is not so great as that stated in our paper; but I feel certain, that with the same delicacy of adjustment and suspension as was formerly given to it by my brother, the former degree of sensibility would be regained.

But first as to Prof. Threlfall's statements and calculations. He says, speaking of the galvanometer of our type which he constructed, and which had a resistance of 15,852 ohms:—"The test for sensitiveness was made by running a large Clark cell through 10,000 legal ohms, and a certain small

resistance taken out of an ordinary bridge-box. The terminals of the bridge-box were coupled up through the galvanometer to a megohm. . . . In the final test the period of vibration of the magnet system was 80 seconds, and the resistance out of the bridge-box was 100 ohms. The E.M.F. acting through the megohm and galvanometer and 100 ohms was therefore $\frac{100}{10100}$ Clark cells, say .0145 volt. The current

was therefore $\frac{.0145}{116000} = 1.26 \times 10^{-7}$ amperes." Lower down

Prof. Threlfall says that this gave a double deflexion of 5 divisions, and that therefore the current per division was " 2.5×10^{-8} amperes."

Now this calculation, if I understand the arrangement (and taking the statement that .0145 volt worked "through a megohm, the galvanometer, and 100 ohms," there seems no room for mistake), is evidently erroneous. The current for the 5 divisions' double deflexion was really $\frac{.0145}{1016000}$ ampere, or

1.43×10^{-8} ampere nearly, and the current per division 2.85×10^{-9} ampere, or 5.7×10^{-9} ampere per division of single deflexion. Thus Prof. Threlfall, by an error in arithmetic, makes the sensibility of his instrument only about $\frac{1}{9}$ of what it was in reality, according to the data which he gives.

For this sensibility it is to be noted the period of vibration of the needle system was 80 seconds, the suspension (two silk fibres) 16 centimetres long, and the distance from the galvanometer-mirror to the scale 155 centimetres.

Prof. Threlfall then describes an instrument of another form which he constructed with the coils of the unsuccessful instrument of our form, and begins his next paper with the following statement of its sensibility:—"The galvanometer having been brought to a state of sensitiveness of 5 scale-divisions for 10^{-11} amperes, the measurement of the resistance of the sample of sulphur in question became a tolerably easy matter." One naturally infers from this statement that the sensibility of the galvanometer in the experiments thereafter described was 2×10^{-12} ampere per division of deflexion. However, calculating from the table on p. 472, we find that it was really about 3×10^{-11} ampere per division of *single* deflexion. If a double deflexion is meant in the statement above, this is only about $\frac{1}{7.5}$ of the sensibility stated, or, if a single deflexion is meant, $\frac{1}{15}$ of the sensibility stated. That the instrument was working near the limit of its sensibility seems evident

from the fact stated by the author that the zero was "always on the move."

It is to be noted that in this instrument the suspension was a quartz fibre 85 centim. long, and that the distance of the scale from the mirror appears (p. 466) to have been 3 metres. (Hence for a scale at a distance of 1 metre from the mirror the current for 1 division of single deflexion would be 9×10^{-11} ampere.)

Thus in his comparison of the two instruments Prof. Threlfall evidently states the sensibility of his own instrument as either 15 or 7.5 times its real amount, and certainly makes the sensibility of the trial instrument of our form only about $\frac{1}{5}$ of what it was according to his own observations.

In my own experiments the arrangement was as follows:—A circuit was made of a Daniell's cell (freshly prepared) and two resistances, one of 22,000 ohms and the other of 100 ohms. The terminals of the galvanometer were applied at those of the resistance of 100 ohms. The galvanometer had a free period of 23 seconds, and the double deflexion produced was 88 scale-divisions each $\frac{1}{40}$ of an inch. Hence the current was nearly 1.5×10^{-7} ampere. For one half millimetre single deflexion the current therefore was 2.7×10^{-9} ampere.

To compare this with Prof. Threlfall's result with the same type of instrument, we ought to reduce to a scale 1.5 metre from the mirror. The current for 1 division would then be 1.85×10^{-9} ampere as against 5.7×10^{-9} for Prof. Threlfall's; or, with only 23 seconds period, my instrument has 3 times the sensibility his had with a period of 80 seconds. With the latter period (and that with even a longer period, the instrument can be readily used, I am certain from our former experiments) the current would be about $\frac{1}{12}$ of that stated, or 1.5×10^{-10} ampere per division; that is, the instrument would have about 36 times the sensibility of that made by Prof. Threlfall. The silk fibre was a little less than 3 inches long, and was by no means so fine as it might be made.

A previous set of experiments, after which the fibre was broken down, and the instrument dismounted for resuspension, gave greater sensibility. The electromotive force of the cell used was, however, in that case a little uncertain.

I ought to state that the sensibility of the instrument depends very much on its state of adjustment. As the time at my disposal for these experiments was very limited, and I am not able to apply anything like the degree of skill which my brother used in the management of the instrument, and in the arrangement of a delicate silk-fibre suspension, the sensibility is not now so great as that which we formerly

obtained. Were everything in its former state (and in a little time I hope to put it so), I am confident that our former estimate of the limit of practical sensibility, viz. 1×10^{-11} ampere per division, would be found not far from the truth.

I can only rejoice if Prof. Threlfall, or anyone else, makes an instrument of a higher sensibility. I hold, however, that our instrument possesses special advantages in point of astaticism, steadiness of zero, &c. Its principal disadvantage is its long period of free vibration owing to the large moment of inertia of the needle system. If, however, we were to construct a new instrument, this would be very greatly diminished.

I am, Gentlemen,

University College of N. Wales,
January 1890.

Your obedient Servant,
A. GRAY.

XXII. Notices respecting New Books.

Physics of the Earth's Crust. By the Rev. OSMOND FISHER, M.A., F.G.S., &c. Second Edition, altered and enlarged. 8vo. Pages i-xvi. 1-391. Macmillan and Co., London and New York. 1889.

THIS excellent book comprises a complete and critical digest of the various results of researches made by very many Physicists in the nature and character of observed phenomena and calculated probabilities relating to the structure and conditions of the Crust and Interior of the Earth. Its value, however, is greatly increased by the Author's own observations and calculations, especially as revised and augmented in this Second Edition. A nearly lifelong experience in Geology has afforded the Author good guidance in the application of his mathematical studies, and has been a better basis for his researches than the merely hypothetical data submitted generally to mathematicians wishing to solve such terrestrial problems as come within the limits of Physical Geology. Many diagrams and some plates are given as illustrations.

With reference to the new features of this Second Edition*, it is stated in the Preface that "possible explanations of some of the difficulties left unsolved in the first edition have since occurred to me. Investigations have also been carried on by others, which appear to strengthen and support some of the conclusions already arrived at; these needed to be followed up and embodied. . . . A great part of the book has been rewritten; and, while there are many additions, there are some omissions. Some portions have been omitted because they seem uncalled for in the present state of Geological opinion; and some because they would not have accorded with the results arrived at in the new portions. At the

* The First Edition was published in 1881. See *Phil. Mag.* ser. 5, vol. xv. p. 56.

same time these results appear to be the legitimate deductions from generally received geological data, now for the first time submitted to mathematical treatment. The most important additions will be found in Chapters V., VI., VIII., IX., XV., XVII., XVIII., XX., XXIII., XXV."

I. Underground temperature is the subject of the opening chapter. The general law of its average rise on descent into the earth, and the probability that it does not remain unaltered for all depths, are discussed.

II. Internal densities and pressures. Chief points:—the Earth probably once wholly melted; now consisting of concentric shells; mean and surface densities; internal pressure; numerical value of the densities according to Laplace's and Darwin's laws,—both satisfying the geodetic and astronomical tests, but the former being the most probable expression of the facts; for, "if the densities of the substances in the central parts of the earth are due rather to their intrinsic nature than to condensation by pressure, it is clear that Laplace's law is the more probable representation of the reality; for it must be remembered that, although based upon a supposed relation between density and pressure, it does not necessarily imply that the density is the result of the pressure."

III. The condition of the Interior is next considered. "The question as to whether the Interior of the Earth is at the present time solid or fluid, or partly solid and partly fluid, apart from geological considerations, may be attacked in two ways. The first of these is by inquiring what would be the difference of effect that bodies exterior to it, namely the sun and moon, would have upon the motions of the Earth in either case; and, secondly, by considering the sequence of events according to which a molten globe, such as the Earth once was, may have passed into its present state." In the first case arguments have been based on the phenomena of the Precession of the Equinoxes and the Tides. These are briefly discussed and disposed of in Chapter III., no appreciable tide in the body of the Earth being produced by the attraction of the moon and sun. The change of density on solidification is illustrated by many collected calculations and observations; and the existence of a cooled crust over a molten mass is regarded as possible.

It is then argued that a liquid substratum might dissolve water-gas, according to Henry's law of the absorption of gases by liquids, and that there would be a very considerable quantity of steam emitted from this substratum if it gained access to the atmosphere in volcanos. Moreover, the high temperature of the gases (chiefly water-gas) passing up through the lava would support its temperature, and would also account for amygdulæ in the deep-seated igneous rocks of many dykes. This hypothesis of absorbed gases is regarded as accounting for the alleged absence of bodily tides within the Earth.

Chapter VI., with its text,—“a thin crust implies an energetic substratum,”—goes to prove that this substratum must be affected by convection-currents, upward and downward, according to local

alterations of temperature and level, as the currents are disturbed, producing changes in the motion of the liquid. Hence occur changes of level on the Earth's crust over different areas of surface. It is also remarked that "the extreme slowness with which the accretion of fresh solid matter at the bottom of the crust takes place [the molten substratum dissolving it nearly, but not quite as fast, as it solidifies] would lead us to expect that its constitution would, from the first, be crystalline and not vitreous. In this respect it would differ from erupted igneous rocks, which are in some cases at first vitreous, and in which a crystalline structure is induced by subsequent metamorphism" (page 78).

IV. The crumpling and contortions of strata, and the inequalities of the surface resulting from lateral stresses, are considered in Chapters VII. to X.; and the existence of a yielding, fluid substratum, holding water-gas in solution (that is, a magma in a state of igneo-aqueous fusion), beneath a thin crust (about 25 miles thick), is regarded as proved and in accordance with geological evidence. The conditions of the existence of the water-substance in a gaseous state, in both the primitive and the present stages of the Earth's history, are discussed in Chapter XI. It is explained in Chapter XII. that the crust is not so flexible as to yield by bending and folding only to lateral pressure; but that the yielding must take place through a crushing together and local thickening of the crust. Chapter XIII. comprises the conditions of a disturbed tract, with the formation of a mountain-range and its root, downward protuberance, or equivalent subterranean mass,—also the local results of denudation and sedimentation. Researches with the plumb-line, pendulum, and thermometer are severally considered in their bearings on the condition of mountain-masses and of the crust generally (Chapters XIV.–XVI.). The attraction of mountain-masses, and the rate of increase of temperature within them, are both much less than would be the case if the heavy, hot, molten liquid from below had risen into their anticlines.

Oceanic areas and the suboceanic crust form the subject of Chapter XVII. Oceans occupy depressions, definitely below the spheroidal surface of the Earth; and these have probably resulted from a greater density of the crust (somewhat thicker there than beneath the Continents); the soft substratum being not quite so dense as that beneath the land. The permanency of the ocean-basins is accepted. Prof. Darwin's speculation of the Moon having broken away from the Earth some 50 million years ago is regarded with favour.

The thickness of the crust below the ocean—when the water is one mile deep may be..... 22.15 miles,
two miles „ „ 49.24 „
three „ „ 124.90 „

Its density is also calculated (2.80 to 2.95). At the rare depth of five miles the density might be so great as to allow the crust to lose heat more rapidly and to sink slowly,—as, for instance, near Japan, where the frequent earthquakes may be due to this cause.

The peculiarities of island attraction (gravity) are succinctly explained in Chapter XVIII. The density of the crust in general is 2.68, and that of the fluid substratum 2.96; and the pressure of the crust upon this liquid substratum is about 10,000 tons on the square foot.

In judging the cause and amount of compression in the Earth's crust (Chapter XIX.), the Author thinks that a mean compression of 4 *per cent.* (of the linear dimensions) may have elevated the continents from the sea-level to their present height (p. 260). Cooling of the crust and contraction of the interior may have been causes of the compression,—also, to a slight degree, extravasation, from beneath the crust, of the water now composing the ocean. It is also pointed out by the Author that the expansive magma (with its included water-gas) forced up from below would widen cracks, thus causing some compression; and that such rocks as whinstone and granite when solidifying would swell, as water does in freezing.

V. Chapters XX. to XXIV., appropriately following the discussion of hypotheses and phenomena in the earlier chapters, are rich with facts and inferences concerning Physical Geology. Disturbance of rocks; folding, crumpling, shearing, faulting; fissures, volcanic dykes, mineral veins; geological movements generally; volcanos, volcanic action, and distribution of volcanos, are subjects of great interest and are here well handled by a master. Chapter XXV. gives an interesting speculation as to the origin of ocean-basins,—comprising Prof. Darwin's hypothesis.

VI. At pages 342-381 we have a concise summary of the objects and results of each Chapter in the book, forming a most valuable *résumé*, which both physicist and geologist will fully appreciate. An excellent Index completes this elaborate work.

The careful references to all observers who have treated of the physics of the Earth's crust, and straight-forward expositions of their views, enhance the value of the book; and we may remark that all the different authors and their opinions have been treated in a characteristically considerate and courteous manner.

XXIII. *Intelligence and Miscellaneous Articles.*

ON THE RESISTANCE OF HYDROGEN AND OTHER GASES TO THE CURRENT AND TO ELECTRICAL DISCHARGES, AND ON THE HEAT DEVELOPED IN THE SPARK. BY E. VILLARI.

AN arc-light between carbon points of 1 centim. diameter is well known to be shorter in a horizontal than in a vertical direction; and the arc is somewhat longer in a vertical position with an ascending current than with a descending one, doubtless owing to the greater heat of the anode, which must become more strongly heated when it is uppermost.

Arc-lights were formed in glass bulbs which were filled with dry gases. The carbon electrodes were superimposed in a vertical position, and were then drawn apart from each other until the arc-

light disappeared. Two arc-lights were each time produced in two glass bulbs, one of which was inserted in the circuit. The strength of the current was measured by an ammeter.

The arc was found to be far shorter in hydrogen than in carbonic acid, and in the latter, again, shorter than in air: the ratio of the lengths was about 3.9 : 7.4 : 8.5. In nitrogen, with an ascending current, it is about 7 times as long as in hydrogen, and with a descending current it is 25.7 times as long. With decrease of pressure the arc lengthens in nitrogen, hydrogen, and coal-gas; in the two latter, however, it never attains the same length as that of the arc in air.

With platinum electrodes the lengths of the arcs in carbonic acid, nitrogen, coal-gas, and hydrogen at ordinary pressures were in about the ratio 16 : 19 : 4.6 : 2.8.

The production of heat at the electrodes was determined for various gases with sparks from a Ruhmkorff's inductorium. The electrodes were thermoelements of iron and German silver. The heating was investigated in two globes filled with various gases, in which the distance between the electrodes was almost identical.

The heating of the negative electrode was greater than with the positive: the difference of the heating effect seemed also to be greater in nitrogen than in hydrogen. A globe filled with hydrogen or with nitrogen was next used, through which the induction-spark was passed, and the strength of the current measured by a well insulated galvanometer. The induced discharge was more enfeebled by a layer of hydrogen than by an equally thick one of nitrogen. Moreover equally thick layers of hydrogen and nitrogen enfeebled the discharge as much as columns of water of 99 and 59 millim. respectively.

In order to diminish the induction-current by the same amount, the length of the spark in hydrogen was 33 millim., in nitrogen 48 millim., and in carbonic acid greater than 49 millim. Hence the resistances were in the order—carbonic acid, nitrogen, hydrogen. The heating of the electrodes increases with the rarefaction.

The spark was then made to pass over the bulb of a mercurial thermometer in various gases. The temperature increased more strongly in nitrogen than in hydrogen both for the induction-spark and for the spark from the battery-discharge. The heating with both was much smaller in hydrogen than in nitrogen, so that in passing through hydrogen the discharge has a much smaller electromagnetic and thermal intensity than in passing through nitrogen. By substituting for the spark other resistances the same result was obtained. A layer of nitrogen 47.6 millim. in length enfeebles the intensity of the induced current to the same extent as a layer of hydrogen 36.95 millim. in length; and a layer of carbonic acid 49 millim. in length as much as a spark 33 millim. in length with the battery-discharge. The negative electrode is almost as strongly heated with the discharge in hydrogen as in nitrogen. With the discharge of the condenser it is more heated in nitrogen.

The spark was finally produced in glass tubes which were surrounded by small calorimeters filled with oil of turpentine. Under

similar conditions the spark in hydrogen develops more heat than in nitrogen, which is just the opposite to what occurs in the measurement of temperatures. The same holds also for the discharge of cascade batteries.—*Rendiconti della R. Acc. dei Lincei*, v. p. 730, 1889; *Beiblätter der Physik*, xiii. p. 1016, 1889.

FURTHER INVESTIGATIONS ON THE INERT SPACE IN CHEMICAL REACTIONS. BY O. LIEBREICH.

The phenomenon of the inert space observed and described by the author (*Phil. Mag.* xxiii. p. 468) has been further followed, and a series of experiments with the chloral mixture are described, which are illustrated by figures showing the influence of the surface of the liquid and of the sides of the vessel on the shape of the inert space. It is thus shown that the evaporation of chloroform cannot be the cause of the phenomenon, nor are immersion and convection phenomena sufficient to account for it. The experiments with iodic acid and sulphurous acid were also extended, and it was more especially shown experimentally that the process of the reaction in narrow spaces is retarded, and in spherical spaces occupies a central position. Analogous phenomena were also observed with the use of vessels of rock crystal, so that the alkali of the glass cannot be adduced as the cause for the occurrence of the inert space. The conclusion forces itself that the physical influence of the side and the varying tension of the surface of the liquid play the predominant part. The hypothesis is not inadmissible therefore that the occurrence of every chemical reaction only becomes possible above a certain magnitude of the space in which it occurs. Transferred to biological processes this leads to the conclusion that chemical processes in cells are also bound up with a certain magnitude of the cells, unless a process of a different kind occurs, which in a certain sense may, in comparison with the normal, be regarded as a degenerative one.—*Sitzungsberichte der Akad. der Wiss. zu Berlin*, 1889, p. 169; *Beiblätter der Physik*, xiii. p. 998, 1889.

LECTURE EXPERIMENT TO PROVE THE EXISTENCE OF THE DIRECT AND INVERSE EXTRA CURRENTS. BY M. C. DAGUENET.

The existence of the direct and inverse extra currents may be easily demonstrated by means of a Wheatstone's bridge. In one of the branches is inserted a high linear resistance, an incandescent lamp for instance, while in the other is a long coil of wire of small resistance. When the normal state of the current is attained the resistances are balanced; then the circuit is opened or closed, and the needle is seen to be deflected either in one direction or the other under the influence of the extra currents, and then return quickly to its position of equilibrium. This experiment is more easily made than that either of Faraday or of Edlund, especially for the current on closing.—*Journal de Physique*, viii. p. 285, 1889.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

MARCH 1890.

XXIV. *The Form of Newton's Rings.* By A. W. FLUX,
B.A., Fellow of St. John's College, Cambridge*.

THE following essay deals with the formation of the equations of Newton's Rings, when the inclination of the surfaces concerned in their formation is taken into account, not merely with regard to its effects in producing a gradually varying thickness of the intervening medium, but also in deflecting the rays so that, though parallel at incidence, they are no longer so on emergence.

Owing chiefly to the finite size of the sources of light available, in spite of the use of the best collimating instruments, the incident light is not a single plane wave, but consists of an infinite series of such waves having their fronts inclined at small angles. Each incident wave will produce a series of colour-effects at any point in the field of view, but these are in general masked by the effects due to other waves; only in the neighbourhood of a certain surface does there exist distinct coloration. The main result of the calculations of this paper is the determination of the surface on which the colour-effects are most clearly defined. This has been effected both for reflected and for transmitted light.

The conclusions arrived at are the following:—

(1) The rings lie on a certain ruled surface of the third order, which cuts the planes through the central spot parallel

* Communicated by the Author.

and perpendicular to the plane of incidence, in two straight lines, which cross each other without intersecting.

We shall refer to these lines as the "Principal" line and the "Transverse" line.

(2) The rings are the curves in which this ruled surface is intersected by a set of coaxial cylinders, which are oblique cylinders on circular bases.

In the case of the transmitted system the rings are not rigidly coaxial, though for ordinary angles of incidence the defect could only be detected by means of very refined instruments.

(3) The rings are symmetrical with regard to the first of the two planes mentioned in (1), both in shape and distinctness.

(4) The principal line being inclined to the surfaces of the plate of glass used in producing the rings, after the ring of a determinate order, every ring will lie partially above the upper surface of the plate. Similarly every ring beyond another determinate limit will lie partly below the lower surface.

(5) The points of the principal line are always clearly defined. In all other directions the clearness varies with the incidence, decreasing as the angle of incidence increases, in general.

Every ring whose order does not exceed a certain limit, determinate for each angle of incidence, will have, however, a pair of points quite clearly defined. These points lie symmetrically on the side of the rings furthest from the incident light. Further, the rings are always more clearly defined on this side than on the other.

(6) Any point in a certain line intersecting the principal and transverse lines, and lying between these lines, may be taken as the central spot, which is therefore, to that extent, indeterminate.

The analytical methods of this paper are, for the most part, derived from an article in Band xii. of Wiedemann's *Annalen der Physik und Chemie*, by Herr Wangerin. Experimental evidence supporting the theory may be found in the first article in that volume.

The results attained by Wangerin are in all respects identical with those of this paper. I have endeavoured to profit by some changes in Herr Wangerin's method, developed in later articles, and to modify these and combine them so as to derive a method which seemed to me to be satisfactory.

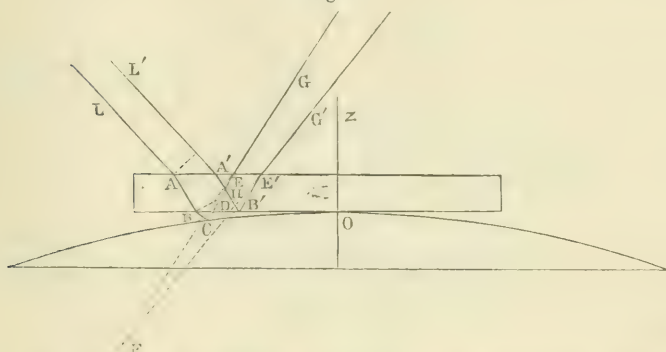
The results for transmitted light have been given by Herr Gumlich in Band xxvi. of Wiedemann's *Annalen*.

PART I.—NEWTON'S RINGS IN REFLECTED LIGHT.

Section I. *Calculation of the Relative Retardations.*

Suppose a plate of plane parallel glass to be in contact at the point O (fig. 1) with the surface of a lens, whose upper surface is convex and of radius r .

Fig. 1.



Let d be the thickness of the glass, μ its refractive index.

Let $L A B C D E G$ be the course of a ray incident on the plate at A and reflected at the lens at C .

Let $L' A' B' E' G'$ be the course of a ray belonging to the same incident wave-front and reflected at the lower face of the plate at B' .

Suppose the pair of rays so chosen that their directions after emergence intersect at the point F .

Let the interval between plate and lens be supposed to contain the same medium (air) as the space above the plate.

Let O be taken as origin, the common normal to lens and plate, drawn on the side towards the plate, as axis of z , and let axes of x and y be taken in the lower face of the plate.

Take

ξ, η, ζ as coordinates of F .

ξ_1, η_1, ζ_1 „ „ C .

ξ_2, η_2, ζ_2 „ „ B .

$u, v, 0$ „ „ B' .

Let

l, m, n be the direction-cosines of AL or CB ,

l_1, m_1, n_1 „ „ „ BA or $B'A'$,

l', m', n' „ „ „ CD ,

l'_1, m'_1, n'_1 „ „ „ DE .

Then

$$\begin{array}{llll} -l_1, -m_1, n_1 & \text{will be the direction-cosines of } B'E'. \\ -l, -m, n & \text{,, ,, ,, } E'G', \\ l', m', n' & \text{,, ,, ,, } EG. \end{array}$$

If we refer C to spherical coordinates with the radius through O as polar axis, ϕ, ψ being those coordinates,

$$\left. \begin{array}{l} \xi_1 = r \sin \phi \cos \psi, \quad \eta_1 = r \sin \phi \sin \psi. \\ \zeta_1 = -r + r \cos \phi = -2r \sin^2 \frac{\phi}{2} = -\frac{r\phi^2}{2}, \text{ q. p.} \end{array} \right\} \quad (\text{i.})$$

The normal at C has direction-cosines,

$$\begin{aligned} & \sin \phi \cos \psi, \quad \sin \phi \sin \psi, \quad \cos \phi. \\ \therefore \quad & l' = -l + 2U \sin \phi \cos \psi, \\ & m' = -m + 2U \sin \phi \sin \psi, \\ & n' = -n + 2U \cos \phi; \end{aligned}$$

where

$$\begin{aligned} U &= l \sin \phi \cos \psi + m \sin \phi \sin \psi + n \cos \phi \\ &= l \phi \cos \psi + m \phi \sin \psi + n \left(1 - \frac{\phi^2}{2}\right) \text{ to the 2nd order;} \end{aligned}$$

$$\therefore \quad \left. \begin{array}{l} l' = -l + 2n\phi \cos \psi + 2\phi^2 \cos \psi [l \cos \psi + m \sin \psi], \\ m' = -m + 2n\phi \sin \psi + 2\phi^2 \sin \psi [l \cos \psi + m \sin \psi], \\ n' = n + 2\phi [l \cos \psi + m \sin \psi] - 2n\phi^2. \end{array} \right\} \quad (\text{ii.})$$

We have also

$$\begin{aligned} l_1 &= l/\mu, \quad m_1 = m/\mu, \quad n_1 = \sqrt{\mu^2 - 1 + n^2}/\mu, \\ l'_1 &= l'/\mu, \quad m'_1 = m'/\mu, \quad n'_1 = \sqrt{\mu^2 - 1 + n'^2}/\mu. \end{aligned}$$

Whence

$$\left. \begin{aligned} \frac{1}{n'_1} &= \frac{1}{n_1} \left[1 - \frac{2n}{\mu^2 n_1} (l \phi \cos \psi + m \phi \sin \psi) + \frac{2n^2}{\mu^2 n_1^2} \phi^2 \right. \\ &\quad \left. + \frac{2}{\mu^2 n_1^2} \left[\frac{3n^2}{\mu^2 n_1^2} - 1 \right] (l \phi \cos \psi + m \phi \sin \psi)^2 \right], \\ \text{and} \quad \frac{1}{n'} &= \frac{1}{n} \left[1 - \frac{2}{n} (l \phi \cos \psi + m \phi \sin \psi) + 2\phi^2 \right. \\ &\quad \left. + \frac{4}{n^2} (l \phi \cos \psi + m \phi \sin \psi)^2 \right]. \end{aligned} \right\} \quad (\text{iii.})$$

Again,

$$u = \xi - \frac{l}{n} (d - \zeta) + \frac{l_1}{n_1} d = \xi + \frac{l}{n} (\zeta - \delta_1),$$

$$v = \eta - \frac{m}{n} (d - \zeta) + \frac{m_1}{n_1} d = \eta + \frac{m}{n} (\zeta - \delta_1),$$

where

$$\delta_1 \equiv d \left[1 - \frac{n}{\mu n_1} \right].$$

And

$$\xi_1 = \xi + \frac{l'}{n'} (d - \zeta) - \frac{l'_1}{n'_1} d - \frac{l'}{n'} 2r \sin^2 \frac{\phi}{2},$$

$$\eta_1 = \eta + \frac{m'}{n'} (d - \zeta) - \frac{m'_1}{n'_1} d - \frac{m'}{n'} 2r \sin^2 \frac{\phi}{2}.$$

Inserting the above expressions for the various direction-cosines in terms of l, m, n, ϕ, ψ , and writing

$$d \left[1 - \frac{n^3}{\mu^3 n_1^3} \right] \equiv \delta_2,$$

we have, to the 2nd order of ϕ ,

$$\left. \begin{aligned} \xi_1 &= \xi + \frac{l}{n} (\zeta - \delta_1) - 2\phi \cos \psi (\zeta - \delta_1) - \frac{2l}{n^2} (\zeta - \delta_2) \\ &\quad (l\phi \cos \psi + m\phi \sin \psi) + \frac{l}{n} 2r \sin^2 \frac{\phi}{2} \\ &= u - 2\phi \cos \psi (\zeta - \delta_1) - \frac{2l}{n^2} (l\phi \cos \psi + m\phi \sin \psi) \\ &\quad (\zeta - \delta_2) + \frac{1}{2} \frac{l}{n} r \phi^2; \\ \eta_1 &= v - 2\phi \sin \psi (\zeta - \delta_1) - \frac{2m}{n^2} (l\phi \cos \psi + m\phi \sin \psi) \\ &\quad (\zeta - \delta_2) + \frac{1}{2} \frac{m}{n} r \phi^2. \end{aligned} \right\} \text{(iv.)}$$

Comparing these values with those in equations (i.), we find that, to the first order,

$$r\phi \cos \psi = u, \quad r\phi \sin \psi = v. \quad \dots \quad \text{(v.)}$$

Using this approximation in the terms of 2nd order,

$$\left. \begin{aligned} \phi \cos \psi &= \frac{u}{r} - \frac{2u}{r^2} (\zeta - \delta_1) - \frac{2l}{n^2} \frac{lu + mv}{r^2} (\zeta - \delta_2) + \frac{1}{2} \frac{l}{n} \frac{u^2 + v^2}{r^2}, \\ \phi \sin \psi &= \frac{v}{r} - \frac{2v}{r^2} (\zeta - \delta_1) - \frac{2m}{n^2} \frac{lu + mv}{r^2} (\zeta - \delta_2) + \frac{1}{2} \frac{m}{n} \frac{u^2 + v^2}{r^2}. \end{aligned} \right\} \text{(vi.)}$$

Also, from the figure,

$$\xi_2 = \xi_1 + \frac{1}{2} \frac{l}{n} r \phi^2, \quad \eta_2 = \eta_1 + \frac{1}{2} \frac{m}{n} r \phi^2. \quad \text{(vii.)}$$

Now, if a plane be drawn through B, perpendicular to BA and B'A' and cutting the latter in H, the vibration in the two rays will be in the same phase at B and H.

If, then, Δ denote the retardation of phase at F of the vibration in FE, relative to that in FE',

$$\left. \begin{aligned} \Delta &= BC + CD + \mu DE - EF - [\mu HB' + \mu B'E' - E'F'] \\ &= 2r \sin^2 \frac{\phi}{2} \left[\frac{1}{n} + \frac{1}{n'} \right] + \mu d \left[\frac{1}{n_1} - \frac{1}{n_1'} \right] + (d - \zeta) \left[\frac{1}{n} - \frac{1}{n'} \right] - \mu HB'. \end{aligned} \right\} \text{(viii.)}$$

Now

$$\begin{aligned} \mu BH' &= \mu [l_1 (\xi_2 - u) + m_1 (\eta_2 - v)] \\ &= l \left[\xi_1 - u + \frac{1}{2} \frac{l}{n} r \phi^2 \right] + m \left[\eta_1 - v + \frac{1}{2} \frac{m}{n} r \phi^2 \right]. \end{aligned}$$

Inserting the values of ξ_1 and η_1 in (iv.) and using in (viii.) the values in (iii.) of $\frac{1}{n_1}$ and $\frac{1}{n_1'}$, and the values of $\phi \cos \psi$, $\phi \sin \psi$ in (vi.), we deduce from (viii.) the following:—

$$\left. \begin{aligned} \Delta &= nr \phi^2 + 2n (\zeta - \delta_1) \frac{u^2 + v^2}{r^2} + \frac{2}{n} \left[\frac{lu + mv}{r} \right]^2 (\zeta - \delta_2) \\ &= n \frac{u^2 + v^2}{r} - 2n (\zeta - \delta_1) \frac{u^2 + v^2}{r^2} - \frac{2}{n} \left[\frac{lu + mv}{r} \right]^2 (\zeta - \delta_2) \\ &\quad + (lu + mv) \frac{u^2 + v^2}{r^2}. \end{aligned} \right\} \text{(ix.)}$$

Correct to the third order, inclusive.

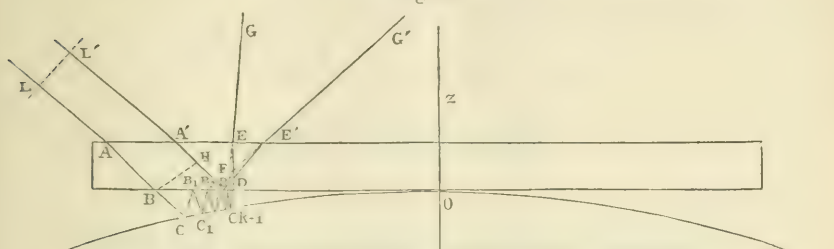
This is the result obtained in equation (8) p. 211, Band xii. of the *Annalen der Physik*.

Section II. *The same in the general case.*

Before proceeding to the use of the evaluation of the retardation in Sect. I., we shall determine in a similar manner

theretardation when one of the rays $A B C B_1 C_1 \dots C_{k-1} D E G$ (fig. 2) is reflected k times at the surface of the

Fig. 2.



lens, and $k-1$ times at the lower surface of the plate, the other ray being only reflected at B' as before.

Take now

ξ, η, ζ as coordinates of F ,
 ξ_r, η_r, ζ_r „ of C_{r-1} [$r < k$],
 ξ', η', ζ' „ of B ,
 $u, v, 0$ „ of B' .

Let the spherical coordinates of $C, C_1 \dots C_r \dots$ be ϕ, ψ ;
 $\phi_1, \psi_1 \dots; \phi_r, \psi_r \dots$;
 and let

l_r, m_r, n_r be the direction-cosines of $C_{r-1}B_r$.

Then

$-l_r, -m_r, n_r$ are the „ of $C_r B_r$.

Let

l', m', n' be the direction-cosines of BA and $B'A'$;

$-l', -m', n'$ are those of $B'E'$.

l'_k, m'_k, n'_k „ of DE .

$-l, -m, n$ „ of FG' .

l_k, m_k, n_k „ of FG .

Also

$$l_k = \mu l'_k, \quad m_k = \mu m'_k, \quad \sqrt{\mu^2 - 1 + n_k^2} = \mu n'_k.$$

If we write down the coordinates of B_1 , deriving them from the coordinates of C first, and then from those of C_1 , we obtain

$$r \sin \phi \cos \psi + \frac{l_1}{n_1} 2r \sin^2 \frac{\phi}{2} = r \sin \phi_1 \cos \psi_1 - \frac{l_1}{n_1} 2r \sin^2 \frac{\phi_1}{2},$$

$$r \sin \phi \sin \psi + \frac{m_1}{n_1} 2r \sin^2 \frac{\phi}{2} = r \sin \phi_1 \sin \psi_1 - \frac{m_1}{n_1} 2r \sin^2 \frac{\phi_1}{2}.$$

∴ To the first order,

$$\phi \cos \psi = \phi_1 \cos \psi_1, \quad \phi \sin \psi = \phi_1 \sin \psi_1.$$

And therefore to the second order,

$$\phi_1 \cos \psi_1 = \phi \cos \psi - \frac{l}{n} r \phi^2,$$

$$\phi_1 \sin \psi_1 = \phi \sin \psi - \frac{m}{n} r \phi^2.$$

Similarly, we have

$$\phi_2 \cos \psi_2 = \phi_1 \cos \psi_1 + \frac{l_1}{n_1} \phi_1^2 = \phi \cos \psi - 2 \frac{l}{n} \phi^2,$$

$$\phi_2 \sin \psi_2 = \phi_1 \sin \psi_1 + \frac{m_1}{n_1} \phi_1^2 = \phi \sin \psi - 2 \frac{m}{n} \phi^2.$$

And, generally,

$$\left. \begin{aligned} \phi_k \cos \psi_k &= \phi \cos \psi - k \cdot \frac{l}{n} \phi^2, \\ \phi_k \sin \psi_k &= \phi \sin \psi - k \cdot \frac{m}{n} \phi^2. \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (i.)$$

Recalling the results of (ii.) section I., we have :—

$$\begin{aligned} l_2 &= l_1 + 2n_1 \left[\phi \cos \psi - \frac{l}{n} \phi^2 \right] - 2\phi_1^2 \cos \psi [l_1 \cos \psi + m_1 \sin \psi] \\ &= -l + 4n\phi \cos \psi - 2l\phi^2 + 8\phi \cos \psi [l\phi \cos \psi + m\phi \sin \psi]; \\ m_2 &= -m + 4n\phi \sin \psi - 2m\phi^2 + 8\phi \sin \psi [l\phi \cos \psi + m\phi \sin \psi]; \\ n_2 &= n + 4[l\phi \cos \psi + m\phi \sin \psi] - 8n\phi^2 - 2 \frac{1-n^2}{n} \phi^2. \end{aligned}$$

Proceeding thus, we find that

$$\left. \begin{aligned} l_k &= -l + 2k n \phi \cos \psi - k(k-1)l\phi^2 \\ &\quad + 2k^2 \phi \cos \psi [l\phi \cos \psi + m\phi \sin \psi], \\ m_k &= -m + 2k n \phi \sin \psi - k(k-1)m\phi^2 \\ &\quad + 2k^2 \phi \sin \psi [l\phi \cos \psi + m\phi \sin \psi], \\ n_k &= n + 2k [l\phi \cos \psi + m\phi \sin \psi] - 2k^2 n \phi^2 \\ &\quad - k(k-1) \frac{1-n^2}{n} \phi^2 + 2 \frac{k^2}{n} [l\phi \cos \psi + m\phi \sin \psi]^2. \end{aligned} \right\} \quad (ii.)$$

Whence

$$\left. \begin{aligned} \frac{1}{n_k} &= \frac{1}{n} \left[1 - \frac{2k}{n} (l\phi \cos \psi + m\phi \sin \psi) + 2k^2\phi^2 \right. \\ &\quad \left. + k(k-1) \frac{1-n^2}{n^2} \phi^2 + \frac{2k^2}{n^2} (l\phi \cos \psi + m\phi \sin \psi)^2 \right]; \\ \frac{1}{n_{k'}} &= \frac{1}{n'} \left[1 - \frac{2nk}{\mu^2 n'^2} (l\phi \cos \psi + m\phi \sin \psi) + \frac{2n^2}{\mu^2 n'} k^2 \phi^2 \right. \\ &\quad \left. + \frac{1-n^2}{\mu^2 n'^2} k(k-1) \phi^2 + \frac{2k^2}{\mu^2 n'^2} \left(\frac{3n^3}{\mu^2 n'^2} - 1 \right) (l\phi \cos \psi + m\phi \sin \psi)^2 \right]. \end{aligned} \right\} \quad (\text{iii.})$$

Also, from the coordinates of C_{k-1} ,

$$\begin{aligned} r \sin \phi_{k-1} \cos \psi_{k-1} &= \xi + \frac{l_k}{n_k} (d - \zeta) - \frac{l_{k'}}{n_{k'}} d - \frac{l_k}{n_k} 2r \sin^2 \frac{\phi_{k-1}}{2}; \\ r \sin \phi_{k-1} \sin \psi_{k-1} &= \eta + \frac{m_k}{n_k} (d - \zeta) - \frac{m_{k'}}{n_{k'}} d - \frac{m_k}{n_k} 2r \sin^2 \frac{\phi_{k-1}}{2}. \end{aligned}$$

Whence, by means of (i.), (ii.), and (iii.),

$$\left. \begin{aligned} \phi \cos \psi &= \frac{u}{r} - 2k \frac{u}{r^2} (\zeta - \delta_1) - \frac{2k}{n^2 r^2} l(lu + mv) (\zeta - \delta_2) + (k - \frac{1}{2}) \frac{l}{n} \frac{u^2 + v^2}{r^2}; \\ \phi \sin \psi &= \frac{v}{r} - 2k \frac{v}{r^2} (\zeta - \delta_1) - \frac{2k}{n^2 r^2} m(lu + mv) (\zeta - \delta_2) + (k - \frac{1}{2}) \frac{m}{n} \frac{u^2 + v^2}{r^2} \end{aligned} \right\} \quad (\text{iv.})$$

We have also

$$\left. \begin{aligned} \xi' &= \xi + \frac{l_k}{n_k} (d - \zeta) - \frac{l_{k'}}{n_{k'}} d + \frac{r}{2} \left[\phi^2 \left(\frac{l}{n} - \frac{l_1}{n_1} \right) \right. \\ &\quad \left. + \phi_1^2 \left(-\frac{l_1}{n_1} - \frac{l_2}{n_2} \right) + \dots \text{to } k \text{ terms} \right] \\ \eta' &= \eta + \frac{m_k}{n_k} (d - \zeta) - \frac{m_{k'}}{n_{k'}} d + \frac{r}{2} \left[\phi^2 \left(\frac{m}{n} - \frac{m_1}{n_1} \right) \right. \\ &\quad \left. + \phi_1^2 \left(-\frac{m_1}{n_1} - \frac{m_2}{n_2} \right) + \dots \text{to } k \text{ terms} \right]. \end{aligned} \right\} \quad (\text{v.})$$

Drawing the plane BH, perpendicular to BA and B'A' as before, the retardation at F of the vibration in FE relative to that in FE' is

$$\Delta_k = BC + CB_1 + \dots + C_{k-1}D + \mu d \left[\frac{1}{n_{k'}} - \frac{1}{n'} \right] + (d - \zeta) \left[\frac{1}{n} - \frac{1}{n_k} \right] - \mu B'H. \quad (\text{vi.})$$

And

$$\begin{aligned} \mu \cdot B'H &= \mu l_1 (\xi' - u) + \mu m_1 (\eta' - v) \\ &= l (\xi' - u) + m (\eta' - v) \end{aligned}$$

Also

$$\left. \begin{aligned} BC + CB_1 + \dots + C_{k-1}D &= \frac{r}{2} \left[\phi^2 \left(\frac{1}{n} + \frac{1}{n_1} \right) + \phi_1^2 \left(\frac{1}{n_1} + \frac{1}{n_2} \right) + \dots k \text{ terms} \right]. \end{aligned} \right\} \quad (\text{vii.})$$

Using the values obtained in (ii.), (iii.), (iv.), (v.), (vii.) in evaluating Δ in (vi.) we obtain

$$\left. \begin{aligned} \Delta_k &= nrk\phi^2 + 2k^2n \frac{u^2 + v^2}{r^2} (\zeta - \delta_1) + \frac{2k^2}{n} \left(\frac{lu + mv}{r} \right)^2 (\zeta - \delta_2) \\ &\quad - k(k-1) \frac{u^2 + v^2}{r^2} (lu + mv), \\ &= kn \frac{u^2 + v^2}{r} - k^2 \left[2n \frac{u^2 + v^2}{r^2} (\zeta - \delta_1) \right. \\ &\quad \left. + \frac{2}{n} \left(\frac{lu + mv}{r} \right)^2 (\zeta - \delta_2) - (lu + mv) \frac{u^2 + v^2}{r^2} \right]. \end{aligned} \right\} \text{(viii.)}$$

Section III. Determination of the Equations of the Rings.

If we now determine the axes of x and y so that the plane xz is parallel to the incident light, and if θ be the angle of incidence,

$$l = \sin \theta, \quad m = 0, \quad n = \cos \theta.$$

Also

$$\delta_1 = d \left[1 - \frac{\cos \theta}{\mu \cos \theta_1} \right], \quad \delta_2 = d \left[1 - \frac{\cos^3 \theta}{\mu^3 \cos^3 \theta_1} \right],$$

where

$$\sin \theta = \mu \sin \theta_1, \quad u = \xi + \tan \theta (\zeta - \delta_1), \quad v = \eta.$$

And with this simplification

$$\begin{aligned} \Delta_k &= k \cos \theta \frac{u^2 + v^2}{r} - \frac{k^2 \cos \theta}{r^2} [2(u^2 + v^2)(\zeta - \delta_1) \\ &\quad + 2u^2 \tan^2 \theta (\zeta - \delta_2) - u \tan \theta (u^2 + v^2)]. \end{aligned} \text{(i.)}$$

We shall find it convenient to refer the system to a new origin and new axis of z , keeping the axis of x and y parallel to the directions just chosen.

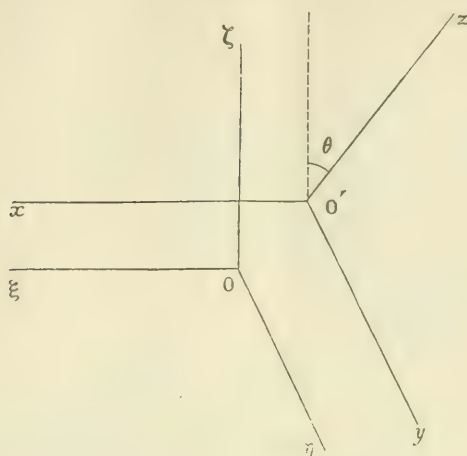
The new axis of z is inclined at an angle θ to its old direction, *i. e.* is parallel to the emergent light which has been but once reflected at the surface of the plate. The new origin is the point $(\xi_0 \zeta_0)$, where

$$\xi_0 = -d(\mu^2 - 1) \tan^3 \theta_1, \quad \zeta_0 = d \left[1 - \frac{\cos^3 \theta}{\mu \cos^3 \theta_1} \right]. \quad \text{(ii.)}$$

The formulæ of transformation are :—

$$\left. \begin{aligned} \xi &= \xi_0 + x - z \sin \theta, \\ \eta &= y, \\ \zeta &= \zeta_0 + z \cos \theta. \end{aligned} \right\} \text{(iii.)} \quad \text{(See fig. 3.)}$$

Fig. 3.



We shall also write

$$z_1 \cos \theta = (\delta_2 - \delta_1) \sin^2 \theta = d \frac{\mu^2 - 1}{\mu^3 \cos^3 \theta_1} \cos \theta \sin^2 \theta;$$

$$i.e. z_1 = \frac{\mu^2 - 1}{\mu^3 \cos^3 \theta_1} d \sin^2 \theta = d \frac{(\mu^2 - 1) \tan^2 \theta_1}{\mu \cos \theta_1}. \quad (iv.)$$

With the assistance of this change of symbols, we shall consider the retardations of systems of incident rays slightly inclined to the incident rays hitherto considered.

If ϕ be the angle between such rays (ϕ being small) and ψ the angle which the plane through the two rays makes with the plane xz , we have

$$\left. \begin{aligned} l &= \sin \theta - \cos \theta \cdot \phi \cos \psi, \\ m &= \phi \sin \psi, \\ n &= \cos \theta + \sin \theta \cdot \phi \cos \psi. \end{aligned} \right\} \quad \dots \dots (v.)$$

$$\mu^2 n_1^2 = \mu^2 - 1 + n^2 = \mu^2 \cos^2 \theta_1 + 2 \sin \theta \cos \theta \cdot \phi \cos \psi + \dots$$

$$\therefore \frac{1}{\mu n_1} = \frac{1}{\mu \cos \theta_1} \left[1 - \frac{\sin \theta \cos \theta}{\mu^2 \cos^2 \theta_1} \phi \cos \psi \right].$$

∴ The new value of δ_1 ,

$$\begin{aligned}\delta_1' &= d \left[1 - \frac{n}{\mu n_1} \right], \\ &= d \left[1 - \frac{\cos \theta}{\mu \cos \theta_1} (1 + \tan \theta \cdot \phi \cos \psi) \left(1 - \frac{\sin \theta \cos \theta}{\mu^2 \cos^2 \theta_1} \phi \cos \psi \right) \right] \\ &= d \left[1 - \frac{\cos \theta}{\mu \cos \theta_1} \right] - d \frac{\cos \theta}{\mu \cos \theta_1} \phi \cos \psi \tan \theta - \left[\frac{\sin \theta \cos \theta}{\mu^2 \cos^2 \theta_1} \right], \\ &= \delta_1 - d \frac{\sin \theta (\mu^2 - 1)}{\mu^3 \cos^3 \theta_1} \phi \cos \psi, \\ &= \delta_1 - \frac{z_1}{\sin \theta} \phi \cos \psi, \quad \dots \dots \dots \text{(vi.)}\end{aligned}$$

$$\begin{aligned}u &= \xi + \frac{l}{n} (\zeta - \delta_1'), \\ &= \xi_0 + x - z \sin \theta + \tan \theta \left(1 - \frac{\phi \cos \psi}{\sin \theta \cos \theta} \right) \\ &\quad (\zeta_0 + z \cos \theta - \delta_1 + z_1 / \sin \theta \cdot \phi \cos \psi), \\ &= x + \phi \cos \psi \left[\frac{z_1}{\sin \theta} - \frac{z}{\sin \theta} - \frac{d(\mu^2 - 1) \tan^3 \theta_1}{\sin^2 \theta} \right] \tan \theta, \\ &= x - \frac{z}{\cos \theta} \phi \cos \psi. \quad \dots \dots \dots \text{(vii.)}\end{aligned}$$

$$\begin{aligned}v &= \eta + \frac{m}{n} (\zeta - \delta_1'), \\ &= y + \frac{\phi \sin \psi}{\cos \theta} (z + z_1) \cos \theta = y + (z + z_1) \phi \sin \psi \quad \dots \text{(viii.)}\end{aligned}$$

Therefore

$$\begin{aligned}\Delta_k' &= \frac{k}{r} (\cos \theta + \sin \theta \cdot \phi \cos \psi) \left[x^2 + y^2 \right. \\ &\quad \left. - \frac{2xz}{\cos \theta} \phi \cos \psi + 2y(z + z_1) \phi \sin \psi \right] \\ &\quad - \frac{k^2 \cos^2 \theta}{r^2} \left[2(x^2 + y^2)(z + z_1) \right. \\ &\quad \left. + 2x \tan^2 \theta (z - z_1 \cot^2 \theta) - \frac{x \tan \theta}{\cos \theta} (x^2 + y^2) \right]\end{aligned}$$

to the 3rd order of small quantities, x, y, z, z_1, ϕ being of the 1st order;

$$\begin{aligned}&= \Delta_k + \frac{k}{r} \left((x^2 + y^2) \sin \theta - 2xz \right) \phi \cos \psi \\ &\quad + \frac{k}{r} \cdot 2y(z + z_1) \cos \theta \cdot \phi \sin \psi, \\ &= A + B \phi \cos \psi + C \cdot \phi \sin \psi \text{ (say)}. \quad \dots \dots \dots \text{(ix.)}\end{aligned}$$

This expression varies least from its mean value A , as ϕ and ψ vary, the former from zero to a small value, the latter from 0 to 2π , when $B^2 + C^2$ is least, *i. e.* when

$$B \cdot \frac{\partial B}{\partial z} + C \cdot \frac{\partial C}{\partial z} = 0,$$

i. e.

$$2x [(x^2 + y^2) \sin \theta - 2xz] - 4y^2 \cos^2 \theta (z + z_1) = 0,$$

or

$$x (x^2 + y^2) \sin \theta - 2x^2 z - 2y^2 \cos^2 \theta (z + z_1) = 0,$$

or

$$2 (x^2 + y^2) (z + z_1) \cos^2 \theta + 2x^2 \sin^2 \theta (z - z_1 \cot^2 \theta) - x \sin \theta (x^2 + y^2) = 0. \quad (x.)$$

When (x.) holds, the value of Δ_k in (i.) becomes

$$\Delta_k = \frac{k}{r} \cos \theta (u^2 + v^2),$$

i. e. the A of equation (ix.)

$$= k \cos \theta \frac{x^2 + y^2}{r} = k\delta, \text{ where } \delta = \frac{\cos \theta}{r} (x^2 + y^2). \quad (xi.)$$

With this value, corresponding closely with that given in the ordinary theory of Newton's Rings, we can determine the equations of those rings at once. The ordinary methods used for thin plates by Glazebrook or Airy furnish the result that the equations are (for the dark rings):—

$$\frac{\cos \theta}{r} (x^2 + y^2) = h\lambda,$$

$$i. e. \quad x^2 + y^2 = \frac{hr\lambda}{\cos \theta} = a^2 \text{ (say)}. \quad (xii.)$$

i. e. The rings lie on this set of coaxial elliptic cylinders.

They also lie on the surface of the 3rd order (x.).

The principle which we have employed to determine the position of the rings is both simple and satisfactory. Though any pair of intersecting rays received into the eye may be regarded as producing interference-results, yet only such need be considered as have their effect neutralized in the least degree by that of other pairs of interfering rays.

Since, in every case of experiment, the incident light is not a simple plane wave, but consists of many plane waves, only limited in direction by the size of the pupil of the eye or object-glass of the observing-instrument, and therefore in general but little inclined to one another, we shall only be able to observe those colour-effects in which these various waves combine to the most complete extent.

These lie on the surface (x.), where it is intersected by the series of coaxial elliptic cylinders (oblique cylinders on circular bases) (xii.).

Section IV. *The Surface of Interference.*

We have now to examine the surface whose equation is given in (x.) of the last section.

We shall use the form

$$x(x^2 + y^2) \sin \theta - 2x^2z - 2y^2 \cos^2 \theta (z + z_1) = 0 \quad . \quad (i.)$$

The points of the surface which we have to consider are its intersections with

$$x^2 + y^2 = a^2; \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

where

$$a^2 = \frac{hr\lambda}{\cos \theta} \text{ or } \frac{2h+1}{2} \frac{r\lambda}{\cos \theta},$$

according as we are considering dark or bright rings.

Where (i.) is intersected by $y=0$,

$$x \sin \theta - 2z = 0 \quad . \quad . \quad . \quad . \quad . \quad (iii.)$$

The intersection is therefore a straight line through the origin.

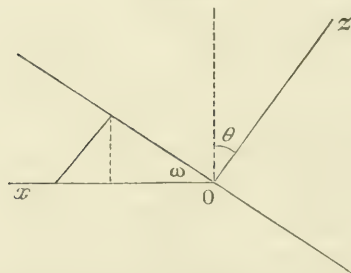
If ω be the angle made by this line with the axis of x ,

$$\sin \theta = \frac{2z}{x} = \frac{2 \sin \omega}{\cos (\theta - \omega)},$$

$$\therefore \tan \omega = \frac{\sin \theta \cos \theta}{1 + \cos^2 \theta} \quad . \quad . \quad . \quad . \quad . \quad (iv.)$$

(See fig. 4.)

Fig. 4.



We may notice that when $\theta=0$ and when $\theta=\frac{\pi}{2}$, $\tan \omega$ vanishes.

It attains a maximum value when $\tan \theta = \sqrt{2}$,

i. e. when $\theta = 54^\circ 44' 8'' \cdot 2$ (about).

For this value $\omega = 19^\circ 28' 16'' \cdot 4$ (about).

This is the greatest value of ω , which varies from zero when θ is zero to this greatest value, and then decreases to zero again as θ approaches a right angle. We notice that the value of ω is entirely independent of the shape, thickness, and material of the lens and plate employed.

The extreme points of any ring in this line are by (ii.) $x = \pm a$.

The actual diameter of the ring is therefore

$$2a \frac{\cos \theta}{\cos (\theta - \omega)} = a \frac{\sin \theta \cos \theta}{\sin \omega} \\ = a \sqrt{1 + 3 \cos^2 \theta}. \quad \dots \quad (v.)$$

The diameter, as seen projected on the horizontal, is the distance from $x = a, z = 0$, to $x = -a, z = 0$, *i. e.* $2a$.

Let us now consider the intersection of (i.) with $y = \pm a$.

Since, so far as the rings are concerned, equation (ii.) is also to be considered, so that $x = 0$, we see from (i.) that

$$z = -z_1,$$

i. e. the intersection of this plane with the ring-system is also a straight line, and, moreover, a line parallel to the surfaces of the glass plate.

We may write (i.) in the form

$$z = \frac{1}{2} \frac{x(x^2 + y^2) \sin \theta}{x^2 + y^2 \cos^2 \theta} - z_1 \frac{y^2 \cos^2 \theta}{x^2 + y^2 \cos^2 \theta} \quad \dots \quad (vi.)$$

Thus, when x and y vanish, z lies between zero and $-z_1$, the exact value depending on the vanishing ratio of x to y .

Thus this portion of the axis of z lies entirely in the surface.

Again, we may write the equation (i.) in the form

$$(x^2 + y^2)(x \sin \theta - 2z) + 2y^2 \sin^2 \theta [z - z_1 \cot^2 \theta] = 0;$$

and hence we see that the line

$$\left. \begin{aligned} z &= z_1 \cot^2 \theta \\ x &= \frac{2z}{\sin \theta} = \frac{2z_1 \cos^2 \theta}{\sin^3 \theta} \end{aligned} \right\} \quad \dots \quad (vii.)$$

lies wholly in the surface.

This is a line parallel to the axis of y .

If we take a plane

$$x \sin \theta - 2z + \lambda (z - z_1 \cot^2 \theta) = 0$$

passing through the line (vii.), it cuts the surface in the pair of straight lines

$$\frac{y}{x} = \pm \sqrt{\frac{\lambda}{2 \sin^2 \theta - \lambda}}.$$

It cuts the axis of z where

$$z = z_1 \cot^2 \theta \frac{\lambda}{\lambda - 2}.$$

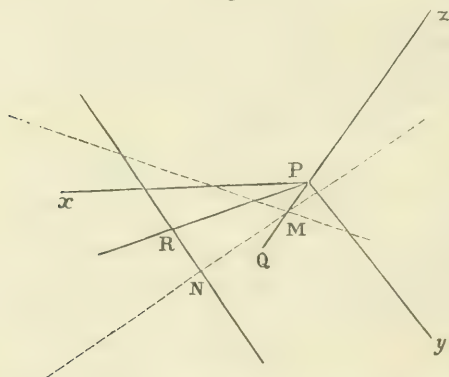
Denoting this value of z by z_0 , we see that

$$\frac{y}{x} = \pm \sec \theta \sqrt{\frac{-z_0}{z_1 + z_0}}$$

gives the pair of lines in which the above plane meets the surface.

It appears, therefore, that the surface is generated by pairs of lines intersecting the axis of z between the origin and $z = -z_1$, and also intersecting the line (vii.). If we denote the origin by P (fig. 5), $z = -z_1$ by Q, and $z = -z_0$ by M,

Fig. 5.



and also the line (vii.) by RN, R being its intersection with the plane xz , and N its intersection with one of the above pair of lines,

$$\begin{aligned} RN &= \frac{2z_1 \cos^2 \theta}{\sin^3 \theta} \cdot \pm \sec \theta \sqrt{\frac{PM}{MQ}} \\ &= \pm \frac{2 \cos \theta}{\sin^3 \theta} PQ \sqrt{\frac{PM}{MQ}}, \end{aligned}$$

giving the law of the generators.

Section V. *Some Points about the Rings.*

From these details concerning the "surface of interference" we may learn something about the rings.

It is evident that since the plane xz cuts the rings in a straight line inclined to the surfaces of the plate, we shall, by proceeding far enough in either direction, at last reach rings which lie partially above or partially below the plate.

The upper surface of the plate is

$$\begin{aligned} z &= (d - \zeta_0) \sec \theta \\ &= d \sec \theta - z_1. \end{aligned}$$

The lower surface is $z = -z_1$.

Hence the line (iii.) in the last section intersects the upper surface of the plate where

$$x = \frac{2(d - z_1 \cos \theta)}{\sin \theta \cos \theta} = \frac{2d \cos^2 \theta}{\mu \sin \theta \cos^3 \theta_1};$$

and the lower surface where

$$x = \frac{-2z_1}{\sin \theta} = -2d \frac{\mu^2 - 1}{\mu^3 \cos^3 \theta_1} \sin \theta,$$

since the order of the ring in this direction ($y=0$) is given by

$$\begin{aligned} x &= \pm a = \pm \sqrt{\frac{h\lambda r}{\cos \theta}} \text{ for the dark rings,} \\ &= \pm \sqrt{\frac{(2h+1)\lambda r}{2 \cos \theta}} \text{ for the bright rings.} \end{aligned}$$

If
$$h > \frac{4d^2}{\lambda r} \frac{\cos^5 \theta}{\mu^2 \sin^2 \theta \cos^6 \theta_1},$$

the dark ring of order h has points above the upper surface of the glass plate.

If
$$h > \frac{4d^2}{\lambda r} \frac{\cos^5 \theta}{\mu^2 \sin^2 \theta \cos^6 \theta_1} - \frac{1}{2},$$

the bright ring of order h lies partially above the upper surface of the glass plate.

If
$$h > \frac{4d^2}{\lambda r} \frac{(\mu^2 - 1)^2 \sin^2 \theta \cos \theta}{\mu^6 \cos^6 \theta_1},$$

the dark ring of order h lies partially below the lower surface of the glass plate; and if $h + \frac{1}{2}$ be greater than the quantity

just written, the bright ring of order h lies partly below the glass plate.

If we denote the line (iii.) of the last section, viz.:

$$\left. \begin{aligned} x \sin \theta - 2z &= 0 \\ y &= 0 \end{aligned} \right\},$$

the principal line, and the plane

$$x \sin \theta - 2z = 0,$$

the principal plane.

The rings lie wholly below the principal plane so long as

$$z < \frac{x \sin \theta}{2}.$$

The greatest value of z determined from equations (i.) and (ii.) of the last section is less than $\frac{x \sin \theta}{2}$ so long as

$$a^2 < 4d^2 \frac{(\mu^2 - 1) \cos^4 \theta}{\mu^6 \sin^2 \theta \cos^6 \theta_1};$$

i. e.

$$h < \frac{4d^2}{\lambda r} \frac{(\mu^2 - 1) \cos^5 \theta}{\mu^6 \sin^2 \theta \cos^6 \theta_1}.$$

It will be observed that this value of h and the first two of those just given is greater as θ is smaller and decreases as θ increases.

It is otherwise with the number determining the order of ring lying below the lower surface of the glass plate.

It was found that the axis of z lies entirely in the surface between $z=0$ and $z=-z_1$.

Thus there arises a certain degree of indeterminateness with regard to the central black spot, any point between these limits being seen with equal clearness. This difficulty is actually found in the course of the experiments undertaken in connexion with this more exact theory of Newton's Rings.

Section VI. *Relative Distinctness of Different Portions of the Ring-system.*

We shall now consider where and under what conditions the rings are formed most distinctly.

In Sect. III. (ix.) the expression found for the retardation was

$$\begin{aligned} \Delta_k' &= A + B \phi \cos \psi + C \phi \sin \psi, \\ &= A + \sqrt{B^2 + C^2} \phi \cos (\psi - \alpha), \text{ where } \tan \alpha = \frac{C}{B}. \end{aligned}$$

When $B^2 + C^2$ is a minimum,

$$A = \frac{k}{r} \cos \theta (x^2 + y^2).$$

$$\text{Also} \quad B = \frac{k}{r} \left[(x^2 + y^2) \sin \theta - 2xz \right],$$

$$C = \frac{k}{r} 2y \cos \theta (z + z_1).$$

We have hitherto not considered the effect of the term involving ϕ , but since the minimum of $B^2 + C^2$ is not always zero, we cannot pass these terms over without notice.

When $y=0$, and $x \sin \theta - 2z=0$, B and C vanish, and therefore the points on the line in the plane xz are always formed clearly.

The only reason why we cannot see rings of a very high order in this plane is that the rings of different colours overlap to such an extent as to obscure the result if the incident light be not strictly monochromatic.

When $x=0$, and $z=-z_1$, C vanishes, but B does not; in fact,

$$B = \frac{k}{r} y^2 \sin \theta,$$

$$= \frac{k}{r} hr\lambda \tan \theta;$$

since $y^2 = a^2 = \frac{hr\lambda}{\cos \theta}$, when $x=0$.

Therefore, the distinctness depends on the magnitude of $h\lambda \tan \theta$. This quantity increases as h increases, and therefore the outer rings in the direction of the axis of y are always less distinct than the inner. Further, as θ increases, $\tan \theta$ increases; and when the incidence is nearly grazing, very few rings can be formed distinctly, since small variations of λ are sufficient to cause large variations of B , and taking also into account the variations of ϕ , the colours overlap so as to cause all trace of variation of intensity or colour to disappear.

Since $B^2 + C^2$ is unchanged by the substitution of $-y$ for y , the rings are equally distinct on the two sides of the plane xz .

Again, since θ lies between 0 and $\frac{\pi}{2}$, when μ is greater than unity (*i. e.* in general) z_1 is positive. Hence

$$(x^2 + y^2) \sin \theta + 2xz_1$$

is decreased by the substitution of $-x$ for x .

Thus the part of the rings on the side of the plane yz which is nearest the incident light is less distinct than the other part.

With the help of the equation of the "surface of interference," we find that

$$\sqrt{B^2 + C^2} = \frac{2y \cos \theta (z + z_1)}{x} \sqrt{x^2 + y^2 \cos^2 \theta}.$$

This vanishes when $(x^2 + y^2 \cos^2 \theta)/x$ vanishes.

Now

$$\begin{aligned} 2(x^2 + y^2 \cos^2 \theta)(z + z_1) &= x[(x^2 + y^2) \sin \theta + 2xz_1] \\ &= x[a^2 \sin \theta + 2xz_1], \end{aligned}$$

$\therefore \sqrt{B^2 + C^2}$ vanishes when

$$x = -\frac{a^2 \sin \theta}{2z_1};$$

and since $x^2 + y^2 = a^2$, this requires that $x \nless a$,

$$i. e. \quad \frac{a \sin \theta}{2z_1} < 1,$$

$$\text{or} \quad h < \frac{4z_1^2 \cos \theta}{\lambda r \sin^2 \theta},$$

$$i. e. \quad h < \frac{4d^2 (\mu^2 - 1)^2 \sin^2 \theta \cos \theta}{\lambda r \mu^6 \cos^6 \theta_1}.$$

For all rings of lower order than the limit so determined there are two points quite distinctly visible, symmetrically situated with regard to the plane xz , and on the side of the plane yz farthest from the incident light.

To obtain the required criterion for bright rings it is only necessary to write $h + \frac{1}{2}$ for h in the above.

If the rings are examined by means of a microscope, the breadth of the visual pencil is much greater than if the naked eye were used. Thus much greater values of ϕ are possible, and the obscurity is consequently increased.

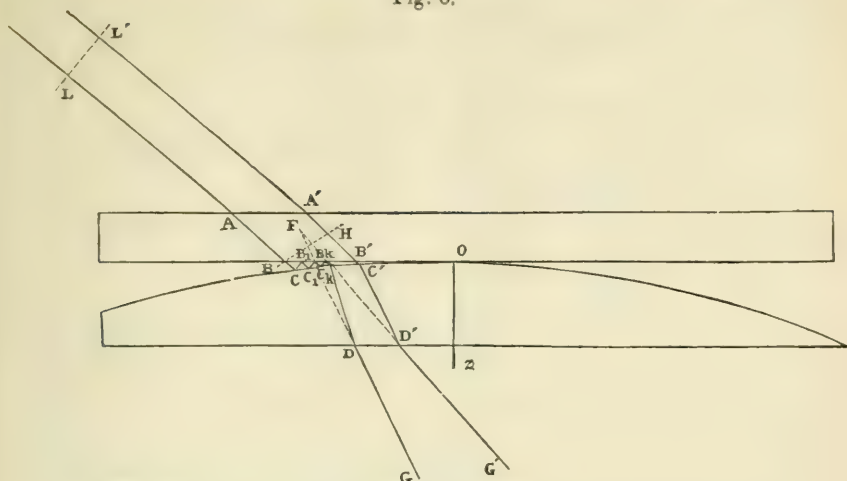
For purposes of exact measurement, however, a microscope is necessary, in spite of the consequent greater indistinctness in the phenomena observed.

PART II.—NEWTON'S RINGS IN TRANSMITTED LIGHT.

Section I. *Calculation of the Relative Retardations.*

We now proceed to consider the case of transmitted light. We shall take the axis of z in the opposite direction from that before used in Part I., viz. drawn towards the side on which the lens lies (fig. 6).

Fig. 6.



The direction-cosines will be similar to those used in Sect. II. Part I., so far as the two cases coincide, viz.:—

The direction-cosines

of LA, L'A', BC, B'C' are $-l, -m, n$;

of AB, A'B' are $-l', -m', n'$;

of B_1C are l_1, m_1, n_1 ; of B_1C_1 are $-l_1, -m_1, n_1$;

&c. &c.

of B_k, C_{k-1} , are l_k, m_k, n_k ; of B_k, C_k are $-l_k, -m_k, n_k$.

Also we shall take as direction-cosines of

C_kD , $-l_{k+1}, -m_{k+1}, n_{k+1}$; $C'D'$, $-\alpha', -\beta', \gamma'$;

FD , $-l_{k+2}, -m_{k+2}, n_{k+2}$; FD' , $-\alpha, -\beta, \gamma$.

The rectangular and spherical coordinates of

C are ξ_1, η_1, ζ_1 , and ϕ, ψ ;

C_1 are ξ_2, η_2, ζ_2 , and ϕ, ψ_1 ;

&c.

C_k are $\xi_{k+1}, \eta_{k+1}, \zeta_{k+1}$, and ϕ_k, ψ_k ;

C' are ξ', η', ζ' , and ϕ', ψ' ;

while F is ξ, η, ζ .

The thickness of the lens at its centre will be denoted by d , while r is the radius of its convex surface. The direction-

cosines of the normal at ϕ, ψ are

$$\sin \phi \cos \psi, \quad \sin \phi \sin \psi, \quad -\cos \phi.$$

We have

$$\left. \begin{aligned} l_{\mathbf{a}} &= l - 2hn\phi \cos \psi + h(h-1)l\phi^2 \\ &\quad - 2h^2\phi \cos \psi [l\phi \cos \psi + m\phi \sin \psi], \\ m_{\mathbf{a}} &= m - 2hn\phi \cos \psi + h(h-1)m\phi^2 \\ &\quad - 2h^2\phi \cos \psi [l\phi \cos \psi + m\phi \sin \psi], \\ n_{\mathbf{a}} &= n + 2h(l\phi \cos \psi + m\phi \sin \psi) - h(h-1) \frac{1-n^2}{n} \phi^2 \\ &\quad + 2 \frac{h^2}{n} [l\phi \cos \psi + m\phi \sin \psi]^2 - 2h^2n\phi^2, \\ \frac{1}{n_{\mathbf{a}}} &= \frac{1}{n} \left[1 - \frac{2h}{n} (l\phi \cos \psi + m\phi \sin \psi) + h(h-1) \frac{1-n^2}{n^2} \phi^2 \right. \\ &\quad \left. + 8h^2 \left(\frac{l\phi \cos \psi + m\phi \sin \psi}{n} \right)^2 + 2h^2\phi^2 \right] \end{aligned} \right\} \quad (\text{i.})$$

Putting

$$\begin{aligned} U &= l \sin \phi' \cos \psi' + m \sin \phi' \sin \psi' + n \cos \phi' \\ &= n + l\phi' \cos \psi' + m\phi' \sin \psi' - n \frac{\phi'^2}{2} + \dots, \\ \alpha' &= -\frac{1}{\mu} [\sin \phi' \cos \psi' \{ \sqrt{\mu^2 - 1 + U^2} - U \} + l], \\ \beta' &= -\frac{1}{\mu} [\sin \phi' \sin \psi' \{ \sqrt{\mu^2 - 1 + U^2} - U \} + m], \\ \gamma' &= +\frac{1}{\mu} [\cos \phi' \{ \sqrt{\mu^2 - 1 + U^2} - U \} + n]. \end{aligned} \quad \left. \right\} \quad (\text{ii.})$$

And

$$\begin{aligned} \alpha &= \mu\alpha', \quad \beta = \mu\beta', \quad \gamma = \sqrt{1 - \mu^2 + \mu^2\gamma'^2}; \\ \therefore \alpha &= l - (n - \mu n')\phi' \cos \psi' - \left(1 - \frac{n}{\mu n'}\right)\phi' \cos \psi' \\ &\quad (l\phi' \cos \psi' + m\phi' \sin \psi'), \\ \beta &= m - (n - \mu n')\phi' \sin \psi' - \left(1 - \frac{n}{\mu n'}\right)\phi' \sin \psi' \\ &\quad (l\phi' \cos \psi' + m\phi' \sin \psi'); \\ \mu^2\gamma'^2 &= \mu^2 - 1 + n^2 - 2(\mu n' - n)(l\phi' \cos \psi' + m\phi' \sin \psi') \\ &\quad - (\mu n' - n)^2\phi'^2 + 2 \frac{\mu n' - n}{\mu n'} (l\phi' \cos \psi' + m\phi' \sin \psi')^2. \end{aligned}$$

Again,

$$\xi - \frac{\alpha}{\gamma} (d - \zeta) + \frac{\alpha'}{\gamma'} (d - \zeta') = \xi' = r\phi' \cos \psi',$$

$$\eta - \frac{\beta}{\gamma} (d - \zeta) + \frac{\beta'}{\gamma'} (d - \zeta') = \eta' = r\phi' \sin \psi'.$$

Therefore, writing

$$u = \xi + \frac{\alpha}{\gamma} (\zeta - \delta_1), \quad v = \eta + \frac{\beta}{\gamma} (\zeta - \delta_1), \quad \dots \quad (\text{iii.})$$

where

$$\delta_1 = d \left[1 - \frac{\gamma}{\mu\gamma'} \right], \quad \delta_2 = d \left[1 - \frac{\gamma^3}{\mu^2\gamma'^3} \right],$$

we have

$$u - \frac{\alpha}{\mu\gamma'} \zeta' = r\phi' \cos \psi',$$

$$v - \frac{\beta}{\mu\gamma'} \zeta' = r\phi' \sin \psi'.$$

$$\therefore r^2 \phi'^2 = u^2 + v^2 - 2 \frac{\alpha u + \beta v}{\mu\gamma'} \zeta';$$

$$\therefore \zeta' = \frac{r\phi'^2}{2} = \frac{1}{2} \frac{u^2 + v^2}{r} - \frac{1}{2} \frac{\alpha u + \beta v}{\mu\gamma'} \frac{u^2 + v^2}{r^2};$$

$$\left. \begin{aligned} \therefore \phi' \cos \psi' &= \frac{u}{r} - \frac{1}{2} \frac{\alpha}{\mu\gamma'} \frac{u^2 + v^2}{r^2} + \frac{1}{2} \frac{\alpha}{\mu^2\gamma'^2} \frac{\alpha u + \beta v}{r} \frac{u^2 + v^2}{r^2}, \\ \phi' \sin \psi' &= \frac{v}{r} - \frac{1}{2} \frac{\beta}{\mu\gamma'} \frac{u^2 + v^2}{r^2} + \frac{1}{2} \frac{\beta}{\mu^2\gamma'^2} \frac{\alpha u + \beta v}{r} \frac{u^2 + v^2}{r^2}. \end{aligned} \right\} \quad (\text{iv.})$$

We shall now proceed to connect ϕ, ψ with ϕ', ψ' .
Writing

$$\delta_1' = d \left[1 - \frac{n}{\mu n'} \right], \quad \delta_2' = d \left[1 - \frac{n^3}{\mu^2 n'^3} \right],$$

$$u_1 = \xi + \frac{l}{n} (\zeta - \delta_1'), \quad r_1 = \eta + \frac{m}{n} (\zeta - \delta_1'),$$

$$\epsilon_h = h - \frac{\mu\gamma'}{\gamma}, \quad \epsilon_h' = h - \frac{\mu n'}{n}.$$

Now $l_{k+2}, m_{k+2}, n_{k+2}$ are derived from l_k, m_k, n_k as α, β, γ are from l, m, n , ϕ', ψ' being replaced by ϕ_k, ψ_k .

Now $\phi_k \cos \psi_k = \phi \cos \psi - k \frac{l}{n} \phi^2,$

$$\phi_k \sin \psi_k = \phi \sin \psi - k \frac{m}{n} \phi^2.$$

Therefore

$$\left. \begin{aligned}
 l_{k+2} &= l_k - (n_k - \mu n_k') \phi_k \cos \psi_k \\
 &\quad - \left(1 - \frac{n_k}{\mu n_k'}\right) \phi_k \cos \psi_k [l_k \phi_k \cos \psi_k + m_k \phi_k \sin \psi_k], \\
 &= l - n \epsilon'_{2k+1} \phi \cos \psi + k \epsilon_k' l \phi^2 - \left[2k^2 + 2k + 1 \right. \\
 &\quad \left. - (2k+1) \frac{n}{\mu n'}\right] \phi \cos \psi (l \phi \cos \psi + m \phi \sin \psi), \\
 m_{k+2} &= m - n \epsilon'_{2k+1} \phi \sin \psi + k \epsilon_k' m \phi^2 - \left[2k^2 + 2k + 1 \right. \\
 &\quad \left. - (2k+1) \frac{n}{\mu n'}\right] \phi \cos \psi (l \phi \cos \psi + m \phi \sin \psi), \\
 n_{k+2}^2 &= n^2 + 2n \epsilon'_{2k+1} (l \phi \cos \psi + m \phi \sin \psi) - 2k \epsilon_k' (1 - n^2) \phi^2 + 2 \left[2k^2 \right. \\
 &\quad \left. + 2k + 1 - \overline{2k+1} \frac{n}{\mu n'}\right] (l \phi \cos \psi + m \phi \sin \psi)^2 - n^2 \epsilon'^2_{2k+1} \phi^2, \\
 l_{k+2} &= \mu l_{k+1}, \quad m_{k+2} = \mu m_{k+1}, \quad \mu n_{k+1} = \sqrt{\mu^2 - 1 + n^2_{k+2}}.
 \end{aligned} \right\} \quad (v.)$$

Therefore

$$\begin{aligned}
 \frac{1}{n_{k+2}} &= \frac{1}{n} \left[1 - \epsilon'_{2k+1} \frac{l \phi \cos \psi + m \phi \sin \psi}{n} + k \epsilon_k' \frac{1 - n^2}{n^2} \phi^2 + \frac{1}{2} \epsilon'^2_{2k+1} \phi^2 \right. \\
 &\quad \left. + \left[\frac{3}{2} \epsilon'^2_{2k+1} - \left[2k^2 + 2k + 1 - \overline{2k+1} \frac{n}{\mu n'} \right] \right] \left(\frac{l \phi \cos \psi + m \phi \sin \psi}{n} \right)^2 \right]; \\
 \frac{1}{n_{k+1}} &= \frac{1}{n'} \left[1 - \frac{n \epsilon'_{2k+1}}{\mu^2 n'^2} + k \epsilon_k' \frac{1 - n^2}{\mu^2 n'^2} \phi^2 + \frac{1}{2} \frac{n^2}{\mu^2 n'^2} \epsilon'^2_{2k+1} \phi^2 + \frac{1}{\mu^2 n'^2} \left[\frac{3}{2} \frac{n^2 \epsilon'^2_{2k+1}}{\mu^2 n'^2} \right. \right. \\
 &\quad \left. \left. - \left(2k^2 + 2k + 1 - \overline{2k+1} \frac{n}{\mu n'} \right) \right] l \phi \cos \psi + m \phi \sin \psi \right)^2 \right].
 \end{aligned}$$

The values of l, m, n in terms of α, β, γ may be deduced from those of α, β, γ in terms of l, m, n .

They are:—

$$\left. \begin{aligned}
 l &= \alpha + \gamma \epsilon_1 \frac{u}{r} + \frac{1}{2} \alpha \left[1 - \frac{\gamma}{\mu \gamma'} \right] \frac{u^2 + v^2}{r^2} - \epsilon_1 \frac{u}{r} \frac{\alpha u + \beta v}{r}; \\
 m &= \beta + \gamma \epsilon_1 \frac{v}{r} + \frac{1}{2} \beta \left[1 - \frac{\gamma}{\mu \gamma'} \right] \frac{u^2 + v^2}{r^2} - \epsilon_1 \frac{v}{r} \frac{\alpha u + \beta v}{r}; \\
 n &= \gamma - \epsilon_1 \frac{\alpha u + \beta v}{r} - \frac{1}{2} \frac{1 - \gamma^2}{\gamma} \left(1 - \frac{\gamma}{\mu \gamma'} \right) \frac{u^2 + v^2}{r^2} \\
 &\quad + \frac{\epsilon_1}{\gamma} \left(\frac{\alpha u + \beta v}{r} \right)^2 - \frac{1}{2} \gamma \epsilon_1^2 \frac{u^2 + v^2}{r^2} - \frac{1}{2} \frac{\epsilon_1^2}{\gamma} \left(\frac{\alpha u + \beta v}{r} \right)^2.
 \end{aligned} \right\} \quad (vi.)$$

$$\mu n' = \mu \gamma' - \epsilon_1 \frac{\gamma}{\mu \gamma'} \frac{\alpha u + \beta v}{r} - \&c.$$

$$\therefore \delta_1' = d \left[1 - \frac{n}{\mu n'} \right] = \delta_1 + \epsilon_1 \frac{\alpha u + \beta v}{\gamma r} (\delta_2 - \delta_1);$$

$$\therefore u_1 = \xi + \frac{l}{n} (\zeta - \delta_1');$$

$$\left. \begin{aligned} \therefore \frac{u_1}{r} &= \frac{u}{r} + \epsilon_1 \frac{u}{r} (\zeta - \delta_1) + \frac{\alpha}{\gamma^2} \epsilon_1 \frac{\alpha u + \beta v}{r} (\zeta - \delta_2), \\ \frac{v_1}{r} &= \frac{v}{r} + \epsilon_1 \frac{v}{r} (\zeta - \delta_1) + \frac{\beta}{\gamma^2} \epsilon_1 \frac{\alpha u + \beta v}{r} (\zeta - \delta_2). \end{aligned} \right\} \text{(vii.)}$$

Again,

$$\left. \begin{aligned} r \phi \cos \psi &= \xi_1 = \xi - \frac{l_{k+2}}{n_{k+2}} (d - \zeta) + \frac{l_{k+1}}{n_{k+1}} (d - \zeta_{k+1}) + \sum_{h=1}^{h=k} \frac{l_h}{n_h} (\zeta_h + \zeta_{h+1}), \\ r \phi \sin \psi &= \eta_1 = \eta - \frac{m_{k+2}}{n_{k+2}} (d - \zeta) + \frac{m_{k+1}}{n_{k+1}} (d - \zeta_{k+1}) + \sum_{h=1}^{h=k} \frac{m_h}{n_h} (\zeta_h + \zeta_{h+1}). \end{aligned} \right\} \text{(viii.)}$$

Using the values already found in (v.) for the direction-cosines, we have

$$\left. \begin{aligned} \phi \cos \psi &= \frac{u_1}{r} - \epsilon'_{2k+1} \frac{u}{r} \frac{\zeta - \delta_1'}{r} - \frac{l}{n^2} \epsilon'_{2k+1} \frac{l u_1 + m v_1 \zeta - \delta_2'}{r} \\ &\quad + \frac{1}{2} \frac{l}{n} \left[2k - \frac{n}{\mu n'} \right] \frac{u_1^2 + v_1^2}{r} \\ &= \frac{u}{r} - 2k \frac{u}{r} \frac{\zeta - \delta_1}{r} - 2k \frac{\alpha}{\gamma^2} \frac{\alpha u + \beta v \zeta - \delta_2}{r} + \frac{1}{2} \frac{\alpha}{\gamma} \left[2k - \frac{\gamma}{\mu \gamma} \right] \frac{u^2 + v^2}{r^2}; \\ \phi \sin \psi &= \frac{v}{r} - 2k \frac{v}{r} \frac{\zeta - \delta_1}{r} - 2k \frac{\beta}{\gamma^2} \frac{\alpha u + \beta v \zeta - \delta_2}{r} + \frac{1}{2} \frac{\beta}{\gamma} \left[2k - \frac{\gamma}{\mu \gamma} \right] \frac{u^2 + v^2}{r^2}. \end{aligned} \right\} \text{(ix.)}$$

And

$$\begin{aligned} \phi_h^2 &= \phi^2 - 2h \frac{\alpha u + \beta v}{\gamma r} \frac{u^2 + v^2}{r^2} \\ &= \frac{u^2 + v^2}{r^2} - 4k \frac{u^2 + v^2}{r^2} \frac{\zeta - \delta_1}{r} - 4k \left(\frac{\alpha u + \beta v}{\gamma r} \right)^2 \frac{\zeta - \delta_2}{r} \\ &\quad + \left[2k - \frac{\gamma}{\mu \gamma} \right] \frac{\alpha u + \beta v}{\gamma r} \frac{u^2 + v^2}{r^2} - 2h \frac{\alpha u + \beta v}{\gamma r} \frac{u^2 + v^2}{r^2}. \end{aligned}$$

ϕ^2 is obtained by putting $h=0$

and

ϕ'^2 is obtained by putting $k=0$ as well as $h=0$.

If a plane be drawn through B perpendicular to B'A' and BA, and cutting the former in H, the points B, H are in the same wave-front which is incident in the direction LA.

Also the coordinates of B' are:—

$$\xi - \frac{\alpha}{\gamma} (d - \zeta) + \frac{\alpha'}{\gamma'} (d - \zeta') + \frac{l}{n} \zeta',$$

$$\eta - \frac{\beta}{\gamma} (d - \zeta) + \frac{\beta'}{\gamma'} (d - \zeta') + \frac{m}{n} \zeta';$$

and those of B are:—

$$\xi_1 + \frac{l}{n} \zeta_1, \quad \eta_1 + \frac{m}{n} \zeta_1;$$

ξ_1, η_1 being given in (viii.).

The difference of path (measured in air) of the two rays, at F is

$$\left. \begin{aligned} & \frac{1}{n} \zeta_1 + \sum_{h=1}^{h=k} \frac{1}{n_h} (\zeta_h + \xi_{h+1}) + \mu \frac{d - \zeta_{k+1}}{n_{k+1}} + \frac{d - \zeta}{n_{k+2}} \\ & - \left[\frac{1}{n} \zeta' + \mu \frac{d - \zeta'}{\gamma'} - \frac{d - \zeta}{\gamma} + \mu B' H \right] \\ & = \frac{1}{n} [\zeta_1 - \zeta'] - \sum_{h=1}^{h=k} \frac{ll_h + mm_h - 1}{n_h} [\zeta_h + \xi_{h+1}] \\ & \quad + \frac{ll_{k+2} + mm_{k+2} - 1}{n_{k+2}} (d - \zeta) \\ & \quad - \frac{ll_{k+1} + mm_{k+1} - \mu}{n_{k+1}} (d - \zeta_{k+1}) - \frac{l\alpha + m\beta - 1}{\gamma} (d - \zeta) \\ & \quad + \frac{l\alpha' + m\beta' - \mu}{\gamma'} (d - \zeta') + \frac{1 - n^2}{n} (\zeta' - \zeta_1). \end{aligned} \right\} \text{(x.)}$$

Now

$$\frac{ll_h + mm_h - 1}{n_h} = -n + 2\text{nd order terms,}$$

and

$$\xi_h + \xi_{h+1} = \frac{r}{2} [\phi_{h-1}^2 + \phi_h^2] = r\phi^2 - (2h-1) \frac{\alpha u + \beta v}{\gamma r} \frac{u^2 + v^2}{r};$$

i. e. is of the 2nd order, and therefore we need not calculate the 2nd order terms in $\frac{ll_h + mm_h - 1}{n_h}$.

Evaluating the other terms by means of equations (iv.) (v.) (vi.) (ix.), we obtain the following result:—

$$\Delta_k = k\gamma \frac{u^2 + v^2}{r} + k \frac{\mu^2 - 1}{\mu\gamma\gamma'} \frac{\alpha u + \beta v}{r} \frac{u^2 + v^2}{r}$$

$$- \frac{k^2\gamma}{r^2} \left[2(u^2 + v^2)(\zeta - \delta_1) + 2 \left(\frac{\alpha u + \beta v}{\gamma} \right)^2 (\zeta - \delta_2) - \frac{\alpha u + \beta v}{\gamma} (u^2 + v^2) \right]$$

as given by Herr Gumlich in Wiedemann's *Annalen*, xxvi. p. 361.

Section II. *The Shape of the Rings.*

The only difference between this expression and that of equation (viii.) of Sect. II. Part I. is in the 2nd term, α, β, γ taking the place of l, m, n .

It is evident that the same process as that adopted in the former part of the paper will give similar results.

Putting

$$\sin \theta = \alpha, \quad 0 = \beta, \quad \cos \theta = \gamma,$$

(θ is the angle of emergence)

the equation of the "surface of interference," referred to a system of axes of which the z -axis is in the direction of emergence, and the substitutions are those of Sect. III. Part I., is

$$x(x^2 + y^2) \sin \theta - 2x^2z - 2y^2 \cos^2 \theta (z + z_1) = 0. \quad \dots (i.)$$

$$\begin{aligned} \therefore \Delta_k &= \frac{k \cos \theta}{r} (x^2 + y^2) + k \frac{\mu^2 - 1}{\mu \cos \theta_1} x \frac{(x^2 + y^2)}{r^2} \tan \theta \\ &= \frac{k}{r} (x^2 + y^2) \cos \theta \left[1 + \frac{x}{r} \frac{\mu^2 - 1}{\cos^2 \theta} \tan \theta_1 \right]. \end{aligned}$$

The other equation to the rings is, therefore,

$$\frac{x^2 + y^2}{r} \cos \theta \left[1 + \frac{x}{r} \frac{(\mu^2 - 1)}{\cos^2 \theta} \tan \theta_1 \right] = h\lambda \text{ or } \frac{2h + 1}{2} \lambda$$

according as we consider the bright or dark rings.

Taking the former and putting a^2 for $\frac{hr\lambda}{\cos \theta}$, this becomes

$$x^2 + y^2 = a^2 \left[1 - \frac{x}{r} \frac{\mu^2 - 1}{\cos^2 \theta} \tan \theta_1 \right]. \quad \dots (ii.)$$

Thus in this case the rings lie on elliptic cylinders which are not co-axial.

The distance of the centre of the h th bright ring from the central spot, from the origin, is

$$\frac{1}{2} a^2 \frac{x}{r} \frac{\mu^2 - 1}{\cos^2 \theta} \tan \theta_1 = \frac{1}{2} h \lambda x \frac{\mu^2 - 1}{\cos^3 \theta} \tan \theta_1.$$

This increases with h and with λ , but is of the order λ^3 unless θ be nearly $\frac{\pi}{2}$, when these differences would become very perceptible. In ordinary cases the difference is not observable, and the rings are practically co-axial.

The shape of the surface of interference is exactly the same as that considered in the earlier part of this paper, and the conditions of distinctness remain unaltered.

December 1889.

XXV. *Twisted Strips.*By Professor JOHN PERRY, *F.R.S.**

IN a paper read at the British Association Meeting this year, and also at a former meeting of the Physical Society, I referred to the curious behaviour of a twisted strip. The twisted strip must not be confounded with what has been called the Ayrton and Perry Spring. It is a straight strip of metal to which a permanent twisted appearance has been given, a twisting moment being applied about the axis of the strip to give it the permanent twist, care being taken to prevent the axis of the strip from lateral motion. In fact the axis remains straight, and is the axis of all the spiral lines now formed by the lines which were originally straight and parallel to the axis. When an axial force is employed to elongate a twisted strip, a slight elongation takes place accompanied by a large relative rotation of the ends of the strip. The only simple hypothesis on which, as I told the Society on a former occasion, I could see my way to building a possible theory was to consider in any very short length of the strip any two spiral filaments equally distant from the axis as two threads in a bifilar suspension. Under the action of any axial force these two threads tend to produce untwisting, and the sum of all these untwisting moments is equal to the torsional rigidity of the cross section multiplied by the angle of untwist.

The phenomena are so complicated that I never hoped to explain them all by this or any other hypothesis. I was seeking for a roughly correct theory only.

The breadth being b and thickness t , we may roughly assume that the section remains rectangular; and as b is always more than ten times t , we may take the torsional rigidity as $\frac{N}{3}bt^3$. If then θ is the angular amount of untwisting produced per unit length of the strip, the moment of torsional resistance is

$$\frac{N}{3}bt^3\theta.$$

Let w be the axial force. If ϕ is the twist of the strip per unit length, then for a filament whose horizontal section is $t \cdot \delta x$, at the distance x from the axis (as t is small compared with b I take the filament as extending quite across the section), if p is the vertical tensile stress on the section, it is

* Communicated by the Physical Society: read November 1, 1889.

obvious that the part of the untwisting moment due to one filament is $t\rho x^2\phi \cdot \delta x$; so that

$$\frac{N}{3}bt^3\theta = t\phi \int_{-\frac{1}{2}b}^{\frac{1}{2}b} \rho x^2 \cdot dx; \quad . \quad . \quad . \quad (1)$$

also

$$w = t \int_{-\frac{1}{2}b}^{\frac{1}{2}b} \rho \cdot dx. \quad . \quad . \quad . \quad (2)$$

I explained on the former occasion that, for a working theory, it ought to be sufficient to take ρ constant over the section. Hence, from (2),

$$\rho = \frac{w}{bt}; \quad . \quad . \quad . \quad (3)$$

and inserting this value in (1), we have

$$\frac{N}{3}bt^3\theta = \frac{1}{2}t\phi b^3 \frac{w}{bt},$$

or

$$\theta = \frac{\phi bw}{4t^3N}. \quad . \quad . \quad . \quad (4)$$

If θ is small in comparison with ϕ , it is allowable to take ϕ as the twist of the strip when no axial load is acting—that is, its permanent twist.

Now I announced on the former occasion that careful experiments made upon large twisted steel strips of various dimensions did not by any means agree with my result. It is true that θ was proportional to w ; but it seemed rather independent of ϕ , and instead of being proportional to b , θ seemed to get less as b was greater; and, again, instead of t^3 in the denominator some power of t between 2 and 3 ought to be taken.

Under these circumstances I asked members of the Society for assistance in obtaining a working theory, but hitherto I have not obtained any.

I wish now to announce that the experiments I referred to, made very carefully by Mr. Still, of the Finsbury College, under my direction, were not sufficiently exhaustive. Mr. C. E. Holland has lately been kind enough to make an experiment for me on a very small strip of platinum silver. He finds that when ϕ is large his results agree very closely with the former results; but as ϕ is made less and less, the law connecting θ and ϕ becomes more and more nearly what is given by (4). The experiments were carried out upon double-twisted strips. That is, a straight strip was taken with its

ends fastened in a frame ; it was caught in the middle and there a twisting-couple was applied, so that one half of it took a right-handed and the other a left-handed permanent twist. Beginning from almost the condition $\phi=0$, by giving more and more permanent twist to the strip and applying loads in each case, it was seen that, for a given axial load, θ was nearly proportional to ϕ at first, but as ϕ became greater and greater the increase of θ was less rapid, θ eventually remaining nearly constant, although ϕ was increased.

I now know that Mr. Still's experiments were carried out upon strips in which there existed so much permanent twist as to resemble the strips in the condition in which they were towards the end of Mr. Holland's twisting operations, and hence θ seemed independent of ϕ .

Now if, instead of taking p constant and using (3), we take p as getting less for filaments at greater distances from the axis, it is obvious that we shall arrive at a result which, although more complicated than (4), will represent much better the results of experiments.

Thus, as is probable enough, if the tensile strain in every filament is such as to keep a section at right angles to the axis parallel to itself, it is easy to show that, instead of p being constant, we must take

$$p = \frac{k}{t(1+x^2\phi^2)} \quad \dots \quad (5)$$

Using this in (2), we find

$$k = \frac{\phi w}{2 \tan^{-1} \frac{1}{2} b\phi}.$$

Substituting (5) in (1) we find, on simplifying,

$$\theta = \frac{3w}{Nt^3} \left\{ 2 \tan^{-1} \frac{1}{2} b\phi - \frac{1}{\phi b} \right\} \quad \dots \quad (6)$$

It is obvious that, except when $b\phi$ is great, (6) becomes

$$\theta = \frac{w}{4Nt^3} \left\{ \phi b - \frac{\phi^3 b^3}{15} + \frac{\phi^5 b^5}{115} \right\}, \quad \dots \quad (7)$$

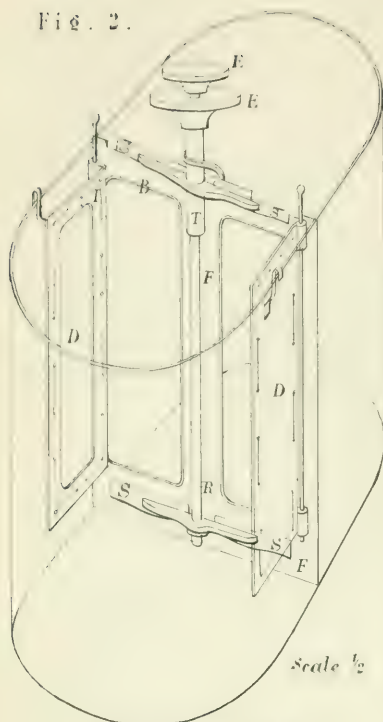
which agrees with (4) for small values of ϕb .

And evidently from (6), as $b\phi$ gets greater and greater, θ reaches more and more nearly the limiting value,

$$\frac{3w}{Nt^3\pi}.$$

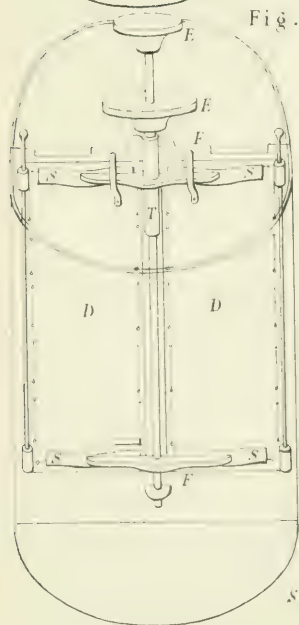
Making p any other likely function of $x\phi$ than that given in (5) will merely modify the constants in (7).

Fig. 2.



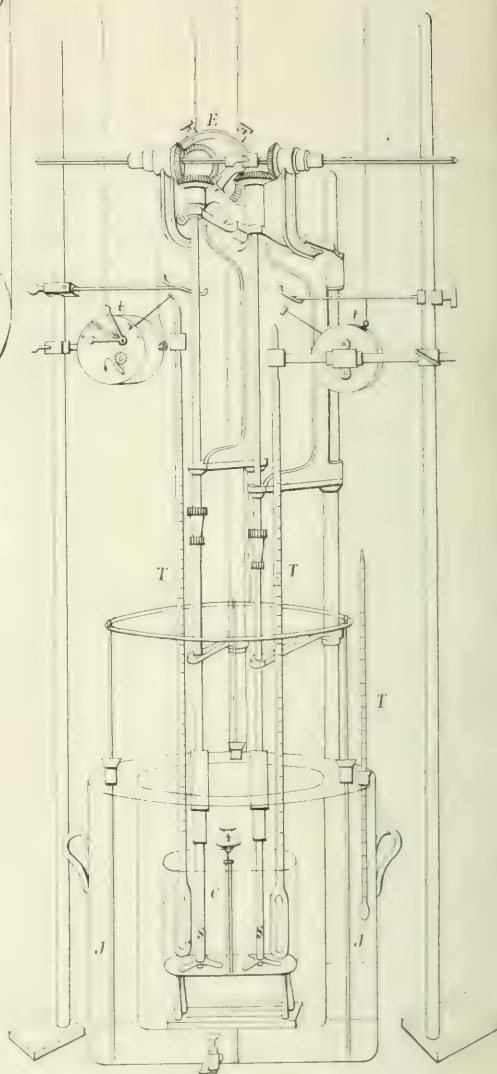
Scale $\frac{1}{2}$

Fig. 1.



Scale $\frac{1}{2}$

Fig. 3.



Scale $\frac{1}{8}$

- T, T, T. Thermometers.
- t, t Thermometer tappers.
- C. Calorimeter.
- S, S. Stirrers.
- J. Double copper water jacket.
- E. Electromotor.

Professor Ayrton and I have used these strips in weighing-machines, instruments in which forces require to be measured, and instruments in which small motions require to be magnified. We are now using the double-twisted strip of constant length, but with initial pull in it, as a thermometer and as a galvanometer. It is my opinion that it only requires to be better known to be largely used; and although I seem to have spent rather in vain a considerable amount of time in trying to get a working theory, I do not think the time has been really wasted. It is no mere curious puzzle, it is a problem of practical importance.

The two great difficulties are—(1) What is the law of p over the section? (2) to what extent is it wrong to regard the section as resisting untwisting with the moment

$$\frac{N}{3} bt^3 \theta ?$$

that is, to what extent has the original twisting given initial shear strains to the material?

XXVI. A New Form of Mixing-Calorimeter.

By SPENCER U. PICKERING, M.A.*

[Plate VII.]

THE methods which have been employed in recent calorimetric work for mixing two liquids are two in number. Berthelot (*Méc. Chim.* i. p. 171) places one liquid in the calorimeter, and adds the other from a flask, which is handled by the help of wooden clips; while Thomsen (*Thermochem. Untersuch.* i. p. 19) has a metal calorimeter for each liquid, one of them being placed above the level of the other, and communicating with the lower one by means of a metal tube, which is stopped by a plug till the temperatures have been ascertained. Berthelot's method is inapplicable in cases where delicate thermometers with large bulbs have to be employed; and there are various other objections both to his and to Thomsen's method, of which the most serious is that the two liquids before being mixed are not at the same temperature, and the results obtained are, therefore, dependent, not only on the accuracy with which the two thermometers have been compared with each other, but also on an accurate knowledge of the heat-capacities of the two liquids.

In devising a new form of mixing-calorimeter, the chief improvement which I aimed at was to obviate this source of

* Communicated by the Author.

error by starting with the two liquids in the same vessel : the other objects to be considered are, however, numerous, and create considerable difficulty in obtaining a satisfactory apparatus. The volumes of the liquids to be mixed are generally required to be equal, and should not exceed 500 cub. centim. in each case : this gives very little spare room, when each liquid contains a thermometer with a large double bulb, and stirrer. No part of the apparatus must be removed, nor must anything be introduced into the liquids to effect the mixing. Whatever operation is necessary to mix the liquids must be performed quickly, so as to avoid the disturbing influence of the experimenter ; and must be consistent with the calorimeter not being held in its position, but with its resting on pointed wooden supports. Finally, the mixing of the liquids must not occupy more than one minute.

The apparatus which I ultimately adopted, after many unsuccessful trials, consisted of an oblong platinum vessel (figs. 1 and 2, Plate VII.), measuring 14 by 8 centim. and 10 centim. deep, with a frame, F, in the middle, against which small folding-doors, D, close, and divide the vessel into two equal compartments. A thin slip of sheet indiarubber, I, is sewn on to the edges of these doors, and a small beading, B, running round the doors and round the partition against which they close, affords a good bedding for the indiarubber, and prevents the leakage, which it was found impossible to obviate when the surfaces of the doors and frame were flat. Each door is kept closed by the pressure of two pairs of bow-shaped pieces of iridio-platinum, S, which act as springs. One of these is at the bottom of the doors, and is attached to a rod, R, of the same alloy, rising vertically above the top of the calorimeter ; the other is at the top of the doors, and is worked by being attached to a metal tube, T, through which the above-mentioned rod passes. The rod and tube each terminate in ebonite knobs, E ; and, when these knobs are pressed together, the lower spring is lowered below the door, while the upper one is raised above it, and the latter consequently opens, and permits the liquids to mix. To allow for the removal of the lower spring in this manner, the doors do not come within 5 or 6 millim. of the bottom of the vessel, and this also allows the stirrer to work freely at the bottom of the liquid.

Under the bottom of the vessel there are four small cup-shaped projections which help to steady it on the pointed supports on which it rests.

The various parts of the apparatus are all distinct, and are easily unscrewed and removed for the purpose of cleaning and drying.

Although the principle of this apparatus is extremely simple, it required the utmost skill in workmanship and the greatest attention to minute details to produce anything which would work really satisfactorily*.

The stirring-apparatus which I use with my single calorimeter consists of a fan-screw with three blades revolving at the bottom of the liquid, and worked by means of an electro-motor (Chem. Soc. Trans. 1887, p. 293). This apparatus was doubled, so that each half of the mixing-calorimeter should have a separate stirrer, and in each half also one of the most delicate thermometers is suspended, these being tapped continuously on the upper end by the clockwork-tapper (*ibid.*). Fig. 3 represents the whole apparatus.

In working this calorimeter it is first of all put in position with the doors closed, and the thermometers and stirrers in their places. The two liquids are then measured or weighed out from flasks into the two compartments, the temperature of each being slightly below that selected for the initial temperature of the experiment. The stirrers and tappers are then started, and the temperature of two liquids raised to the required temperature by touching the outside of the calorimeter with some heated object. The temperatures of the two liquids are in this way easily and quickly brought to within $0^{\circ}\cdot02$ of each other.

The thermometers are then read through a telescope at intervals of one minute, till the rate of cooling in each case is perfectly regular: this occurs in a minute or two, and the temperatures of the liquids may then be assumed to be identical. The rate of cooling is then determined for three or four observations; after which the doors of the calorimeter are opened without stopping the stirrers; the thermometers are again read, and the readings repeated at intervals of one minute, as before, in order to determine the correction for cooling at the final temperature.

Although it is not absolutely necessary to have a thermometer in each liquid, it is not only advisable as a precautionary measure, but it gives the method a very important advantage over previous methods; for the heat evolved being measured independently by two different instruments, a single experiment has nearly the same value as the mean of two separate ones.

The temperature, as has been mentioned, may be obtained identical in each division of the vessel before the doors are

* To the ingenuity and perseverance of W. Peover, of Leigh Street, W.C., I am indebted for success in this work.

opened ; but I have found it convenient, and often necessary, not to wait till absolute identity is attained, but to open the doors when there may be a difference sometimes of as much as $0^{\circ}003$ between the two temperatures. This difference, when unavoidable, was entirely due to local circumstances which are independent of the apparatus itself, chiefly to its position with regard to the windows in the room, one division of it being nearer the window than the other. The correction necessary on account of this difference (often *nil*) is so insignificant that it does not require any knowledge of the heat-capacities of the liquids, and necessitates an accurate comparison of the readings of the two thermometers throughout but a very small portion of their scales (only two or three millimetres), since the initial temperatures in the individual experiments of any series need never differ by more than this amount.

The following details of an experiment will render the method of procedure clear.

Left-hand Division.			Right-hand Division.		
Water. Thermometer '61.			CaCl ₂ sol. Thermometer '08.		
Time.	Reading.	Rate of cooling.	Time.	Reading.	Rate of cooling.
0 0	145.65 mm.*		0 30	151.33 mm.*	
1 0	145.17 "	.48	1 30	151.05 "	.28
2 0	144.90 "	.27	2 30	150.80 "	.25
3 0	144.63 "	.27	3 30	150.60 "	.20
5 30	198.95 "	.60	6 0	195.50 "	.50
6 30	198.35 "	.70	7 0	195.60 "	.50
7 30	197.65 "	.55	8 0	194.50 "	.45
8 30	197.10 "		9 0	194.04 "	

* 1 millimetre represents about $0^{\circ}01$ C.

The rate of cooling here became constant after $1' 0''$. The last reading of the thermometer for the initial temperatures was taken at $3' 30''$, and the doors were opened by $4' 0''$. Up to this time the first-determined rates of cooling would hold good, and the reading of thermometer '61 at this moment would be $[144.9 \text{ (the mean of the three previous readings)} - (.27 \times 2)] = 141.36$ millim.; while that of '08 would be

[$150.82 - (.23 \times 1.5) =$] 150.48 millim. But, according to the previous comparison of the thermometers, the reading of '08 which corresponds to 144.36 of '61 is 150.28 millim.; hence the initial temperatures corrected for this difference will be, according to '08 ($150.48 - .10$) millim., and according to '61, ($144.36 + (.10 \times \frac{1.03}{8.6})$) millim.; the fraction $\frac{1.03}{8.6}$ representing the relative values of 1 millim. of the scale of the two instruments.

The liquids had entirely mixed in this experiment at 5' 0'', and the readings of the two instruments at this moment would be [197.99 (mean of the last four readings) + $(.62 \times 2) =$] 199.23 millim. in the case of '61, and [$194.76 + (.48 \times 2.5) =$] 195.96 millim. in the case of '08. During the one minute while the liquids were mixing, the rate of cooling is taken to be the mean between the rates at the initial and final temperatures, necessitating the further addition of .44 and .36 millim. to the readings last mentioned. The only other corrections to be then applied are those for the effect of the temperature of the surrounding air on the mercurial columns, and the calibration corrections.

Where one liquid is very much more dense than the other, as in mixing water with salt-solutions of a density 1.3 to 1.7, two special difficulties arise: the temperature of the salt-solution rapidly rises to an appreciable extent above that of the water, owing to the greater friction of the stirrer in the former; and, secondly, the two liquids mix very slowly when the doors are opened, taking, in extreme cases, nearly 30 minutes to do so. This latter is not, however, entirely due to the viscous nature of the liquid, but to the fact that the two stirrers in my present apparatus rotate in opposite directions, whereas for the purpose of rapidly mixing the liquids they should rotate in the same direction.

These objections are, however, of no great importance. They do not exist in cases where there is a difference of .2 or less in the densities of the solutions, and in very few cases would the difference reach this amount.

The exactitude of the method may be estimated by the fact that the difference in the rise or fall of temperature as measured by the two thermometers in all the experiments which I have yet performed with the apparatus (omitting those in which the liquids were too dense to mix in less than three or four minutes) is, on the average, only $0^{\circ}.0008$, and only on three occasions did it exceed twice this amount. This quantity represents a sum total of .07 millim. error in all the readings of the two thermometers, and represents a difference of 0.6 cal. in the heat measured, taking the actual quantities used

(on that calculated for gram-molecular proportions); an error only one seventeenth as great as that experienced by Thomsen, its average error in duplicate experiments being ± 5 cal. from the mean, or a difference of 10 cal. between duplicates (*ibid.* i p. 21).

When dealing with very strong solutions it is inadvisable*, and often impracticable, to make the determination in the mixing-calorimeter.

The method which I have adopted in such cases is very simple. It consists of putting 20 to 50 grams of the liquid into test-tubes on feet, placing these in an air-bath surrounded by a water-jacket till they have attained the temperature of the surrounding air, and then pouring their contents into 600 cub. cent. of water in the calorimeter (a platinum beaker); thus the heat of dissolution is determined as in the case of a solid. The chief precaution to be observed here is, that the tubes be left sufficiently long in the air-bath before being emptied into the calorimeter. This is necessary owing to the heat-capacity of a liquid being generally higher than that of a solid, any error in the determination of its temperature making therefore a greater error in the heat of dissolution determined. About three hours in the air-bath at a constant temperature (that is, within $0^{\circ}05$ of the required temperature) were generally allowed, and greater pains were taken to bring this temperature to exactly that of the calorimetric water than in the case of solids. If the temperature of the air in the room is satisfactorily constant, and nearly identical with that in the bath, a comparison of the temperatures of the latter and that of the water in the surrounding jacket will indicate the time when the test-tubes have attained the former (and the latter) temperature; and if left under these constant conditions for nearly another hour, satisfactory results will be obtained. Success in this is entirely a matter of practice. The correction which has to be applied to the heat of dissolution, owing to differences in the initial temperature of the solutions and the calorimetric water, averaged only about $0^{\circ}002$, and the heat-capacity of the strong solutions necessary for its calculation need therefore be known approximately only. All splashing on pouring in the solutions is entirely

* In mixing acids and alkalies the results obtained are more accurate in proportion as the solutions are more dilute. In determining the heat evolved on diluting strong solutions, the experimental errors increase in a very rapid proportion if the determinations are made by diluting the solutions with successively equal volumes of water. Further details will be found in a paper on the Nature of Solutions, in the current number of the Journal of the Chemical Society.

obviated by the use of the wire-gauze tray suspended just below the surface of the water.

When dealing with liquids, where dissolution takes place almost instantaneously, the "uncertain interval" when the temperature is between the initial and final points is practically *nil*, and may be overlooked. The process in making the determination therefore consists in ascertaining the rate of cooling at the "initial temperature," and correcting the last reading of this so as to give its value at the moment of the addition of the solution (15 seconds generally after this last reading), and dating the commencement of the rate of cooling at the "final temperature" from this moment. Three or four readings at intervals of one minute generally suffice to determine this latter rate satisfactorily.

I now invariably read the thermometers without stopping the stirrers and tapping-apparatus, and I believe that greater accuracy in the results is thereby obtained.

XXVII. On Kerr's Magneto-optic Phenomenon.

By H. E. J. G. DU BOIS, of the Hague*.

§ 1. **INTRODUCTORY.**—Dr. Kerr has shown, in 1877, that the mode of vibration of light is in general affected by reflexion from a magnet. Hitherto this phenomenon has been almost exclusively studied from an optical point of view †; in particular, the complicated behaviour of light, obliquely reflected from magnets, has been much discussed. A magnetic curve was, however, given by Prof. Kundt, from which I drew the following conclusion ‡: for light normally reflected, the rotation is probably proportional to the magnetization, as it is for light transmitted through magnets. Starting from this, I have now further investigated the phenomenon

* Translated by the Author from Wied. *Ann.* xxxix. p. 25 (1890); a synopsis of results had been communicated to the British Association, Newcastle. See Proceed. of Sect. A, Sept. 17, 1889 Report.

† Literature:—Kerr, *Phil. Mag.* [5] iii. p. 321 (1877), and v. p. 161 (1878); Kaz, *Dissert.*, Amsterdam (1884); Kundt, Wied. *Ann.* xxiii. p. 228 (1884), and xxvii. p. 198 (1886); Righi, *Ann. de Chim. et Phys.* [6] iv. p. 433 (1885), ix. p. 65 (1886), and x. p. 200 (1887).

Theoretical papers:—Fitzgerald, *Proc. Roy. Soc.* xxv. p. 447 (1876); *Phil. Mag.* [5] iii. p. 529 (1877); *Phil. Trans.* clxxi. p. 691 (1880); Wied. *Ann.* xxv. p. 136 (1885). Rowland, *Phil. Mag.* [5] ix. p. 432 (1880), and xi. p. 254 (1881). H. A. Lorentz, *Versl. en Mededeel. Amsterdam*, xix. p. 217 (1883), and *Arch. Néerl.* xix. p. 123 (1884). van Loghem, *Dissert.*, Leiden, 1883, and Wied. *Beibl.* viii. p. 869 (1884). Voigt, Wied. *Ann.* xxiii. p. 493 (1884). Ketteler, *Theor. Optics*, Brunswick, 1885.

‡ du Bois, Wied. *Ann.* xxxi. pp. 965, 974 (1887).

in its intimate connexion with magnetization. Optical complications were purposely avoided by working at almost normal incidence. I have also determined the effect of temperature, the rotational dispersion, and the characteristic absolute constants.

§ 2. *Method*.—Light from a Linnemann's burner (incandescent zirconia disk) was made to pass horizontally in succession through red glass, a lens, a Lippich's penumbral polarizer; it then reached the vertical mirror of the magnet, by which it was reflected into the analyser and telescope. By special constructive devices the parts of the apparatus, passed through by the light before and after reflexion respectively, could be fixed on a common base so near to each other as to have their optical axes inclined at but 2° ; this angle is halved by what I shall call the apparatus's medial line. The observer's eye was, of course, carefully screened from the burner. The medial line was adjusted normal to the mirror. By this arrangement practically normal incidence (at 1°) was ensured; in fact, Righi* noticed hardly any change in the phenomenon up to 15° of incidence.

The same physicist has found that with plane-polarized light, normally incident, the reflected vibrations are exceedingly oblong ellipses, the azimuth of whose major axis naturally differs from that of incidence. I saw no reason for making measurements of ellipticity; working with a penumbral polarizer, the azimuth of the major axis is what is actually observed. When using good mirrors and avoiding all diffused light, the alternative extinction of each half of the field of vision proved satisfactory, thus showing the ellipticity to be very small. The analyser's azimuth was measured by a modification of Poggendorff's mirror-and-(vertical)-scale method†. The arrangement and dimensions of lenses, diaphragms, the telescope, &c., had been calculated beforehand with a view to obtain the field of vision as bright and uniform as possible.

§ 3. The metallic cores principally used were ovoids (prolate ellipsoids of revolution) of different material, on to which small reflecting-planes had been ground in various positions.

* Righi, *Ann. Chim. et Phys.* [6 sér.] ix. pp. 120 and 132 (1886).

† [This was separately described (*Wied. Ann.* xxxviii. p. 494, 1889) in order not to encumber the present paper with details, and does not pretend to anything beyond a mere laboratory expedient. It has since come to my notice that other experimenters have used similar devices.]

I desire to thank Messrs. Hartmann and Braun, of Bockenheim and Frankfort, and their foreman, Mr. G. Troll, who executed this difficult job for me with perfect success. The ovoids were magnetized in a coil of 1080 turns, 30 centim. long. In order to let light pass, small looking-tubes (.7 centim. diam.) had been fixed between the wire during winding. These lay in meridian planes through the coil's axis, and inclined at various angles to it.

§ 4. Notwithstanding the resulting slight irregularity of winding, the field was sufficiently uniform over the space to be covered by the ovoids. This was tested by the magnetic rotation in bisulphide of carbon, measured at different points on the coil's axis. At the same time the field could thereby be determined in absolute measure; and a numerical factor deduced, by means of which the readings of an amperemeter in the coil's circuit were afterwards reduced to fields. The ovoids' moment was magnetometrically determined in the ordinary manner, the coil's action on the magnetometer being compensated by that of a second coil. Apart from ovoids, I have also worked with small reflecting disks, fixed between the poles of a Ruhmkorff electromagnet. Certain other arrangements will be described in due time.

§ 5. *Notations*, often recurring:— \mathcal{H} , intensity of coil's field; \mathfrak{J} , magnetization, and \mathfrak{J}' , mean magnetization of ovoids; $2a$, $2b$, their major and minor axes; $n=b/a$, axial ratio; \mathfrak{N} , outward normal to mirror; α , angle $\angle(\mathfrak{J}, \mathfrak{N})$. K , Kerr's constant (see § 24); θ , temperature; λ , wave-length; ϵ_0 , rotation on "polar" reflexion; ϵ , rotation (according to § 2 this is to be understood as meaning the angle between the incident rectilinear vibration and the major axis of the reflected ellipse). Of course, 2ϵ was in the first place determined experimentally by reversing the current, generally as a mean of from 10 to 30 observations of azimuth. In every case below, however, the values of ϵ are given in minutes, radian measure being still too little usual in such work. Otherwise, wherever the contrary is not expressly stated, all quantities and scales of diagrams are given in C.G.S. units. Wherever the sense of rotations has to be expressed with reference to vectors, I shall use the system of the vine and European "right-handed screw"*. Accordingly, the sign of Kerr's effect, *e. g.* for iron, is *negative*, the sense of rotation having to be referred to the direction of magnetization.

* Maxwell, Treatise, 2nd ed. i. p. 24.

FIRST PART.

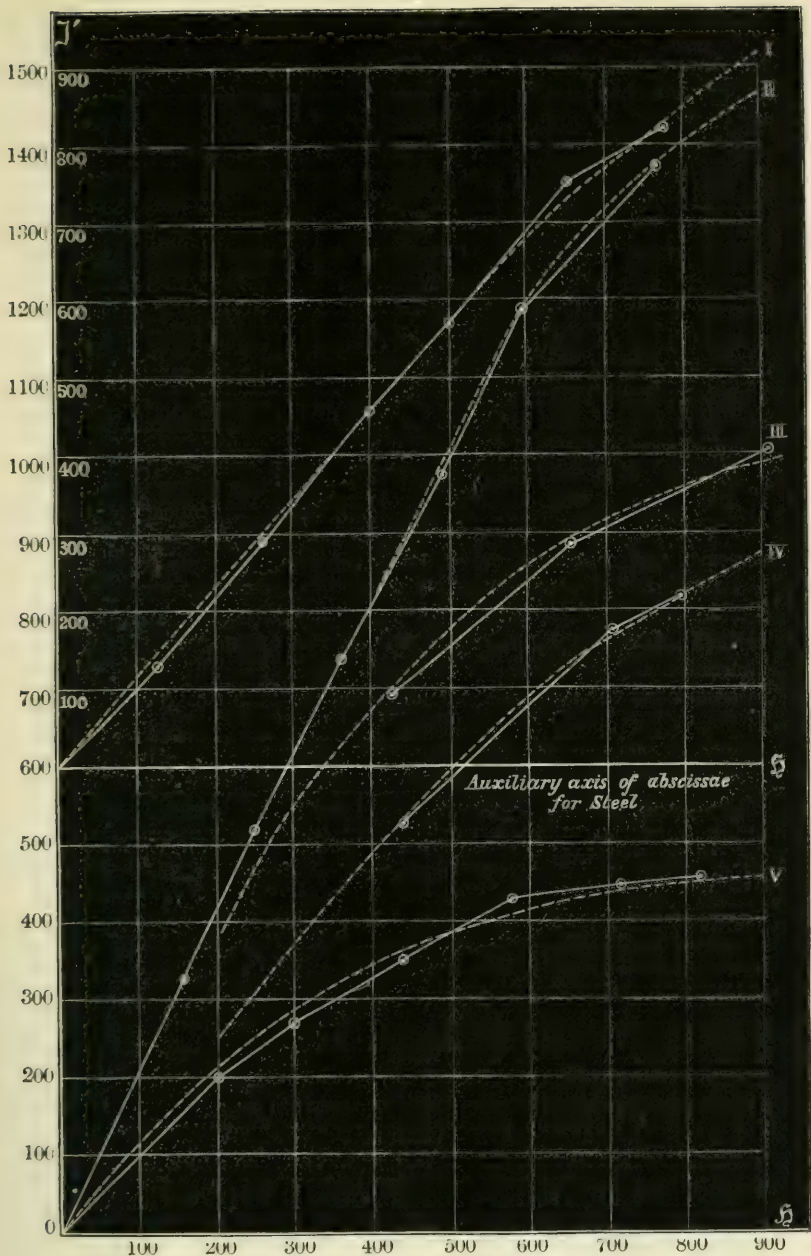
§ 6. I begin by describing the experiments with the ovoids. The polarizer consisted of a nicol and a Hartnack-Prazmowski's semi-prism (see § 16). The zirconia disk stood in the focus of the first lens, which thus projected parallel rays on to the mirror. Distance of vertical scale about 175 centim.

§ 7. *Normal temporary magnetization*.—The 5 ovoids used in this case were provided at one end with circular mirrors perpendicular to the axis of revolution, and were magnetized parallel to the latter. In this case, therefore, the reflexion, according to Dr. Kerr's nomenclature, is "polar," *i. e.* the metal is magnetized normally to the mirror ($\alpha=0$). An ellipsoid (particular cases : sphere, spheroid, ovoid) is known to be the only finite figure in which iron is uniformly magnetized when subjected to a uniform field. In particular, no figure bounded by planes exists, for which this might be the case otherwise than approximately. Instead of such of vanishing size I had to use mirrors whose dimensions were only so far reduced as was consistent with sufficient intensity of the reflected beam. The ovoidal shape was necessarily disfigured by the missing segments ; and the magnetization, uniform on the whole, must be differently distributed in the neighbourhood of the small planes ; it is easy to see that it must be less than with an infinitely small mirror.

§ 8. Some preliminary trials were made to show that this is the correct view of the case. On turning down the mirror of one ovoid successively from $\cdot 7$ to $\cdot 5$ and then to $\cdot 3$ centim. diam., the rotation increased each time, *ceteris paribus*. Another ovoid, provided with mirrors at both ends, showed the lesser rotation at the larger mirror. Lastly, an ovoid was fitted as one pole-piece into an electromagnet, with the result that the rotation, for about the same estimated mean degree of magnetic saturation, proved considerably larger than when the ovoid was magnetized in the coil. The second bored pole-piece acts in the same manner as Kerr's "sub-magnet," *i. e.* it prevents the self-demagnetizing action of the plane end. In the final experiments the observed rotation may be estimated at 60 to 75 per cent. of that which would occur were the mirror of vanishing size (by data of § 19).

§ 9. The rotation, evidently a local action of magnetization, was now directly compared with the magnetometer-deflexion, apparently an action at a distance. The quotient (moment/volume) gives the mean magnetization \mathfrak{J}' of the ovoid, plotted in the broken curves of fig. 1 as a function of

Fig. 1.



- I. Glass-hard English Cast Steel (tempered at 100°),
 $2a=10$; $2b=2$; $n=\frac{1}{2}$.
 II. Soft Swedish Iron (annealed):
 $2a=12.6$; $2b=1.8$; $n=\frac{1}{2}$.

- III. Cast Iron:
 $2a=12.6$; $2b=1.8$; $n=\frac{1}{2}$.
 IV. Cast Cobalt:
 $2a=10$; $2b=2$; $n=\frac{1}{2}$.
 V. Hard-drawn pure Nickel:
 $2a=10$; $2b=2$; $n=\frac{1}{2}$.

the magnetizing field. The rotation ϵ_0 proved very nearly proportional to \mathfrak{J}' ; for each ovoid the mean m of the ratios ϵ_0/\mathfrak{J}' was therefore calculated. By marking the values of ϵ_0/m in the figure, and joining these points \odot , lines are obtained consisting of straight parts nearly coinciding with the broken curves, so as even partly to overlap in the small diagram. Proportionality is now seen to exist between ϵ_0 and \mathfrak{J}' at the first glance. The optical phenomenon, however, can evidently only depend upon the magnetic condition immediately behind the mirror; the following conclusion therefore appears justified: Within the comparatively narrow range of fields applied (\mathfrak{J} between 100 and 900 C.G.S.), the distribution remains unchanged; accordingly, \mathfrak{J} , the magnetization at the mirror, is proportional to \mathfrak{J}' , the mean magnetization throughout the ovoid.

I. *This gives the Law of Proportionality:*

$$\epsilon_0 = K \mathfrak{J},$$

where K is a constant.

In order to give this result a solid experimental foundation I have worked with 5 ovoids of different metals and various axial ratios. Accordingly each curve is seen to exhibit its peculiar character between the extremes of steel and nickel, though in each case verifying the proportionality to be proved.

§ 10. *Inclined temporary magnetization.*—All researches hitherto published refer either to "polar" ($\alpha = 0$) or to "equatorial" ($\alpha = 90^\circ$) reflexion. The case of magnetization inclined to the mirror's normal remains to be investigated. On to a large ovoid ($2a=15$; $2b=3$; $n=1/5$) of soft Swedish iron small elliptical mirrors (minor axes .25 centim.) were ground under different angles to the axis of revolution. These were so small in comparison with the ovoid that the latter's longitudinal magnetization might be considered uniform. Accordingly the rotation observed may be estimated (by data of § 19) at 90 to 95 per cent. of that with an infinitely small mirror. The inclinations of the mirrors to the axis of revolution were measured in the lathe; the angles α are their complements.

§ 11. The rotation was now measured for 4 mirrors with the same current flowing in the coil, and the beam of light passing forwards and backwards through the looking-tubes mentioned in § 3. The value zero for equatorial reflexion at normal incidence is taken from previous observers.

The numbers in the last line were calculated by analogy to Verdet's cosine law. The apparatus for these last experi-

	Polar, ϵ_0 .	Inclined.			Equat.
α	0°	$39^\circ.4$	$50^\circ.5$	$77^\circ.2$	90°
Rotat. observ. ϵ	$-16'5$	$-12'6$	$-9'7$	$-4'6$	0
Rotat. calcul. $\epsilon_0 \cos \alpha$	$-16'5$	$-12'8$	$-10'5$	$-3'7$	0

ments having been difficult to construct, many sources of error occurred; considering these, the observed and calculated values of ϵ sufficiently agree.

II. This leads to the Cosine Law

$$\epsilon = \epsilon_0 \cos (\zeta, \mathfrak{N}).$$

It must still be remarked that the plane parallel to the mirror's normal and to the direction of magnetization may be called a "magnetic principal plane." In the above experiments this principal plane and the plane of polarization of the incident light were both horizontal. Experiments with a cobalt mirror, obliquely magnetized, proved that the same rotation is obtained whether one plane is perpendicular or parallel to the other. The effect is therefore independent of the azimuth of incidence. Equally good extinction was observed with inclined magnetization as on polar reflexion.

§ 12. *Normal residual magnetization.*—In order to obtain this an elongated ovoid ($2a=18$; $2b=1.2$; $n=1/15$) of glass-hard English cast steel, tempered at 100° , had to be used. This, on the other hand, offered the disadvantage that the end was considerably disfigured by grinding on a mirror. The magnetic distribution must therefore differ considerably from a uniform one. I succeeded in obtaining a residual rotation in the shape of a change of the analyser's zero on impressing reversed residual magnetizations; it could be measured as a mean of 30 observations. The influence of magnetic history was each time eliminated after the manner of Gauguain, Auerbach, Maxim, Ewing, and others, by gradually diminishing reversals. Results follow:—

	ζ .	\mathfrak{N} .	ϵ_0 .	$\epsilon_0 \mathfrak{N}$.
Residual	0	180	$-0'6$	$-.0033$
Residual	0	250	$-0'8$	$-.0032$
Temporary	200	570	$-2'8$	$-.0049$

§ 13. On account of the slight rotation no very sharp conclusions can be drawn from these numbers. The ratios of the last column are certainly all of the same order of magnitude; the first two, corresponding to residual rotations, appear to be equal and less than the third. This is easily explained by the plausible assumption of a residual distribution differing from the temporary one in giving comparatively less magnetization near the mirror. The result appears to me to lead to the following interpretation:—

For the law of proportionality it matters not whether the magnetization be residual or kept up by external induction.

This would tend to prove that the rotation is an immediate effect of magnetization and depends upon it alone*.

§ 14. *Effect of temperature.*—The ovoids could be fixed in a brass tube closed at one end, and fitted at the other with a number of diaphragms, through the central apertures of which the mirror remained visible. This tube was heated by a horizontal perforated burner; the necessary draught being obtained by two waterjet-exhausters, which thus acted like chimneys. This arrangement could be introduced inside the coil, separated from it by an asbestos jacket. With a current of 30 amperes the coil and its contents could be electrically heated up to 170° ; by means of the burner the ovoid could be raised to higher temperatures still. Magnetic and optical observations were then made simultaneously during cooling. The rate of cooling could be modified at will by regulating the enclosing coil's temperature by the current. The temperature was given with sufficient approximation by a thermometer having its bulb near the mirror and stem projecting from the apparatus. Of course the metals were heated only for a short time and never beyond the temperature at which they begin to show surface-colours; as the least film of oxide on the mirror completely modifies the phenomena†.

§ 15. The results are given in Table I. The numbers for cobalt, iron, and steel on the whole lead to the conclusion that the value of ϵ_0/\mathfrak{J}' is but little variable with temperature. At the same time \mathfrak{J}' varies so little‡ with θ that the distribution may be safely considered constant. Consequently ϵ_0/\mathfrak{J} ($=K$) is proportional to ϵ_0/\mathfrak{J}' , i. e., by the above, practically constant.

For nickel, however, \mathfrak{J}' diminishes considerably while θ

* du Bois, Wied. *Ann.* xxxi. p. 973 (1887).

† Kundt, Wied. *Ann.* xxvii. p. 199 (1886).

‡ See footnote † next page.

TABLE I.

θ .	ϵ_0 .	\mathfrak{I}' .	ϵ_0/\mathfrak{I}' .	θ .	ϵ_0 .	\mathfrak{I}' .	ϵ_0/\mathfrak{I}' .
Cobalt. $\mathfrak{H}=930$.				Steel. $\mathfrak{H}=930$.			
29°	-10.9	894	-.0121	31°	-10.7	983	-.0109
98	-11.0	894	-.0123	101	-10.8	979	-.0111
167	-11.2	894	-.0126	147	-10.7	964	-.0111
220	-11.2	897	-.0125				
Iron. $\mathfrak{H}=930$.				Nickel. $\mathfrak{H}=820$.			
27°	-13.0	1528	-.0085	27°	-4.9	472	-.0103
78	-12.3	1524	-.0080	99	-5.4	452	-.0118
120	-12.1	1523	-.0080	162	-5.2	426	-.0123
164	-13.6	1517	-.0090 *	245	-4.8	330	-.0146
				282	-3.2	198	-.0163

increases†: the self-demagnetizing action thereby decreases at higher temperatures, so that the distribution approaches to uniformity, and the values of \mathfrak{I} and \mathfrak{I}' tend to become equal. It follows that even if ϵ_0/\mathfrak{I} be constant, ϵ_0/\mathfrak{I}' will none the less increase with θ , and this is what the numbers for nickel actually do. Experiment therefore does not contradict the highly probable assumption that K is practically constant for nickel as well as for the other metals. At temperatures above 280° no more data could be obtained with sufficient accuracy. But on further heating I observed a rapid decrease of both rotation and magnetization until both vanished for temperatures above 335°, only to reappear simultaneously on cooling. This qualitative experiment affords a convincing instance of the close relation between both quantities. The result of this paragraph may be thus expressed:—

III. *The variation of the constant K with temperature is practically zero*; it is certainly less than a few per cent. per 100°, and therefore much below that of the electric resistance

* It is quite possible that a thin colourless film of oxide begins to cover iron about 164°, which would explain the larger rotation here given; the temperature corresponding to a pale yellow is stated to be about 220° on heating for a short time. See Loewenherz, *Zeitschr. f. Instrum. Kunde*, ix. p. 316 (1889). For cobalt, and especially for nickel, these temperatures happen to lie much higher.

† It may not be superfluous to remark that from the values of \mathfrak{I}' given, nothing more than a qualitative conclusion may be drawn as to the thermomagnetic behaviour of the metals; for the self-demagnetizing action of the rather short ovoids tends to diminish any temperature-variations of their magnetization. For quantitative determinations in thermomagnetism the metals have to be used in forms fulfilling the condition of perfect or approximate endlessness.

and index of refraction*. It may also be remarked that Dr. Sissingh† has not been able to observe any change in the two ordinary constants of reflexion for iron between 20° and 120°.

SECOND PART.

§ 16. The experiments in which the electromagnet was used remain to be described. Polarizer and analyser now consisted of genuine Lippich prisms‡. Working with a parallel beam of light was now given up, and an image of the zirconia disk thrown on the analyser's diaphragm instead; by this artifice of Lippich's the disturbing effect of any flickering of the source of light on the accuracy of observation is counteracted. Distance of vertical scale is 400 centim. nearly. These improved arrangements, together with the mounting of the optical apparatus on a pillar, separate from the electromagnet, considerably increase the accuracy of the results stated below above that hitherto attained.

§ 17. *Other active substances.*—Besides the three metals, exhibiting negative rotation on reflexion, I have detected Kerr's effect on common magnetic iron-ore. A piece of loadstone, ground and polished, showed a slight rotation between the poles of an electromagnet. Its numerical value varies over the mirror, but it is always *positive*. For quantitative measurement this material is of no use on account of its heterogeneous structure.

I therefore got a mirror ground parallel to the octaheder (111) of a small crystal of magnetite (Fe_3O_4 , holohedr. tesseral). With a strong current in the electromagnet this gave a rotation $\epsilon_0 = +5'$ for red light; the extinction was perfect, proving the ellipticity to be quite negligible. The rotation proved independent of the azimuth of incidence relatively to the crystal's principal directions; I therefore abstained from having other mirrors ground on in different positions, magnetite evidently behaving like an isotropic body. It would be interesting to observe the effect on transmitted light. However, hitherto I have not been able to find any method of procuring transparent films of this highly opaque substance.

§ 18. I have further tried the following much less magneti-

* Kundt, *Berl. Berichte*, Dec. 1888, p. 1393.

† Sissingh, *Dissert.*, Leiden, 1885, p. 136; *Arch. Néerl.* xx. p. 216 (1886).

‡ Lippich, *Wien. Ber.* xci. 2, p. 1081 (1885). These prisms, as made by Dr. Steeg and Reuter, of Homburg, give a perfectly uniform field of vision with a well-defined line of demarcation; unfortunately, the linseed-oil used in their construction requires months for drying, so that I could not use them from the beginning.

zable, though powerfully absorbent, substances, but without any positive result—sulphide of iron (FeS , amorphous), and oxide of iron (Fe_2O_3 , rhombohedr. hemihedr. hexagonal; mirror normal to principal axis). The fact that a measurable Kerr's effect has hitherto been detected only on the strongly magnetizable opaque substances Co, Ni, Fe, Fe_3O_4 , points once more to the important part which magnetization plays in the phenomenon. I am much obliged to Prof. Bücking for kindly supplying me with these minerals.

§ 19. *Absolute constants.*—After having considerably improved the accuracy of the optical observations, as pointed out in § 16, I could venture to apply them in their turn to magnetic measuring purposes. This application of the law of proportionality I shall describe* in detail; at present I will only mention that by means of it I was able to find the magnetizations corresponding to the rotations ϵ_0 given below. By division the absolute values of the constant K are obtained for “red” light in minutes per unit magnetization.

	Cobalt.	Nickel.	Iron.	Magnetite.
ϵ_0	-20'.97	-7'.25	-22'.99	
\mathfrak{J}	1060	453	1669	
K	-0198	-0160	-0138	+012

The value for magnetite is approximate; the others refer to the massive metals free from oxide; I could not detect any effect due to the polishing material. Thick electrolytic films gave about the same rotation under the same circumstances, but in general this depends on their thickness and surface condition†; such films are, therefore, hardly suited for absolute measurement.

§ 20. *The rotational dispersion* of Kerr's phenomenon is anomalous, but only for iron is it sufficiently developed to interfere with working in white light. For quantitative measurement I applied spectral analysis in connexion with Lippich's‡ penumbral method. By means of a prism “à vision directe” a solar spectrum was thrown on a small screen.

* In the April number of this Magazine.

† See Kundt, Wied. Ann. xxvii. p. 199 (1886).

‡ Lippich, loc. cit. p. 1070; and Wied. Ann. xxxvi. p. 767 (1889).

All parts of this combination were rigidly put together, and its optical axis adjusted perpendicular to the medial line (§ 2) of the optical apparatus. Instead of Lippich's slitted screen a "slitted mirror" of adjustable breadth was set up vertically at 45° to the spectral screen in about the same place where the zirconia disk previously stood. This mirror, therefore, projected a sufficiently homogeneous beam of light into the polarizer.

§ 21. The positions of the lines Li α , D, b , F, G were marked on the spectral screen and checked by means of spectra of Li, Na, and H. The slitted mirror was afterwards set to these. The "red" light used in the preceding experiments was not quite homogeneous, but owing to the slight dispersion sufficiently exact measurements could be made with it. Strictly speaking a definite wave-length cannot be assigned to the "red" light. But in order to allow a reduction of the spectral measurements to absolute values the question arises: which part of the spectrum is rotated through the same angle as was found for the "red" light? To this a definite answer may be given; by trial and interpolation I found for the wave-length $\lambda = 62 \times 10^{-6}$ centim.

§ 22. The rotation was determined with each metal for six colours, each angle being obtained from thirty observations. The values of K (in minutes per unit magnetization) are given in Table II.; the numbers marked with an asterisk are

TABLE II.

Colour.	Line.	$\lambda \times 10^6$ cm.	Cobalt.	Nickel.	Iron.	Magnetite.
Red.	Li α	67.1	-.0208	-.0173*	-.0154	+.0096
"Red."	62	-.0198*	-.0160*	-.0138*	+.0120*
Yellow.	D	58.9	-.0193	-.0154*	-.0130	+.0133*
Green.	b	51.7	-.0179	-.0159	-.0111	+.0072*
Blue.	F	48.6	-.0181	-.0163*	-.0101	+.0026*
Violet.	G	43.1	-.0182*	-.0175*	-.0089	

the means of two separate series of observations. In plotting $K = \text{funct.}(\lambda)$ perfectly continuous curves of dispersion are obtained, showing the following characters:—

IV. *Cobalt has a faintly pronounced minimum for bluish green. Nickel a minimum for yellow. The iron curve runs almost straight down from red to violet. Lastly, for magnetite a maximum occurs in the yellow.*

Unfortunately quantitative observations with the poorly reflecting magnetite could not be pursued beyond blue. Further measurements might have proved the more interesting, as the rotation appeared almost to vanish for violet. I do not deem it impossible that the rotation passes through zero and changes sign in the ultra-violet, though this point appears difficult to decide.

THIRD PART.

§ 23. *The combined expression of both experimental laws, $\epsilon_0 = K\mathfrak{J}$ and $\epsilon = \epsilon_0 \cos(\mathfrak{J}, \mathfrak{N})$, leads to the general law:—*

$$\epsilon = K\mathfrak{J} \cos(\mathfrak{J}, \mathfrak{N}) = K\mathfrak{J}_n,$$

where \mathfrak{J}_n stands for the component magnetization normal to the mirror. This relation was found for red light, but may evidently be extended to radiations of all wave-lengths; it may be thus expressed:—

V. *The rotation of the major axis of vibration of radiations normally reflected from a magnet is algebraically equal to the normal component magnetization, multiplied into a constant K.*

Poisson, as is well known, has shown how any arbitrary magnetic distribution may be replaced, without prejudice to its internal or external action, by fictitious magnetic fluids, distributed in a definite manner throughout the magnet and on its surface*. The surface-density \mathfrak{s} of the latter portion is given by the equation $\mathfrak{s} = \mathfrak{J}_n$. By the above we now have the rotation proportional to the surface-density, and it would thus appear theoretically possible to determine the latter by purely optical means. It would, however, be of no practical use to introduce the fictitious quantity \mathfrak{s} into the physical equation; it has no meaning beyond that of a purely mathematical symbol.

§ 24. The constant K is a quantity of dimension $[L^{\frac{1}{2}} M^{-\frac{1}{2}} T]$ in electromagnetic measure. For four substances it is given in Table II. as a function of the wave-length; it hardly varies with temperature. I venture to propose calling it “Kerr’s constant;” for another quantity, which I have previously defined and denoted Ψ^\dagger , the name “Kundt’s constant”

* Not to be confounded with Gauss’s surface distribution, the action of which may be substituted for that of the magnet only for points external to it. Both distributions do not coincide except in the particular case of solenoidal magnetization.

† The constant Ψ for radiations of definite wave-length is algebraically equal to the rotation which the plane of polarization of such radiations would experience on normal transmission through a plate of unit thickness and unit normal magnetization; du Bois, *Wied. Ann.* xxxi. p. 968 (1887).

appears suited. These names are formed analogously to that of another magneto-optic quantity, viz. "Verdet's constant," which is quite generally accepted; they recall the names of the discoverers of the corresponding phenomena, and are not limited to any particular language. I therefore believe that no objection can be made against their introduction, which appears desirable in order to avoid confusion among three essentially different constants of nature.

§ 25. *Conclusion.*—To my mind the experiments discussed leave no doubt but that the peculiar phenomena connected with reflexion from magnets solely depend upon the magnetization existing immediately behind the mirror; and I believe that no theory ought to ignore this fact. They also supply an experimental proof, which, however, is hardly required, for the assumption that at least part of the incident radiation penetrates below the surface and is there acted upon by magnetism, to be reflected out again afterwards. For, supposing the ray's path to lie entirely outside the metal, the action could only depend upon the magnetic condition of the air, which, however, is not the case.

I have been able to show, on a former occasion, that magnetization also is the quantity upon which the effect on transmission of radiations through magnets depends; this of course is intimately related to Kerr's phenomenon. The latter is doubtless the more complicated of the two phenomena, and differs from the former in sign and in the character of its dispersion*. I believe the following simple kinematical explanation may be given for this difference; in doing so the dynamics of both phenomena are left aside as a remoter question.

§ 26. On normal transmission through a magnetic film the resulting difference of phase between the two opposite circularly polarized rays depends on their different velocity of propagation only; for the geometrical path is the same for both, viz. the film's thickness. On normal reflexion, however, the "optical path"† in the metal (=retardation of phase) is proportional for each ray to the quotient of the geometrical path by the velocity of propagation. Now the latter as well as the geometrical path (in consequence of the different depth

* The rotation is known to be positive on transmission through Co, Ni, and Fe; its dispersion is anomalous, but according to Dr. Lobach (*Dissert.*, Berlin, 1890) it shows neither maxima nor minima.

† "Optical path" = geometrical path \times index of refraction; a convenient expression used by some authors.

of penetration*) is different for the two circular rays. Accordingly it is easily seen that the difference of optical path, and therefore the difference of phase, may have the opposite sign for reflexion or transmission respectively. In fact it is only necessary that the swifter circular ray penetrate so much deeper than the slower one, that the acceleration of phase, which it would otherwise acquire, be thereby changed into a retardation behind the phase of the slower ray.

Generally speaking it is therefore possible that the rotations on reflexion or transmission respectively have the same or opposite signs. The former might even have different signs according to wave-length, and vanish for particular values of λ . Experiment seems to point to a case of this kind with magnetite (§ 22). The curves of dispersion for reflexion and transmission of course need not show any analogy; in any particular case this depends upon the properties of the substance. The above considerations were hinted at by Voigt†, though in a different form; but they are not limited to any particular optical theory, whether electric or elastic. They are of a purely kinematical nature; the hypothesis of circular birefraction and "biabsorption," on which they are based, must, however, be retained.

The contents of this paragraph have therefore to be considered apart from all that precedes; with this sole exception I have striven to cling to experiment and its immediate consequences, free from any additional assumption. In conclusion, I beg to tender my best thanks to Prof. F. Kohlrausch, in whose laboratory these experiments were carried out.

Phys. Inst. of Strasburg Univ.,
Oct. 20, 1889.

* The most general assumption is that part of each circular ray is reflected in the surface itself. The rest then penetrates into the metal, and every elementary sheet of its substance again reflects a "circular element," with amplitude the less, the greater the depth at which reflexion ensues. The reflected pencil now consists of one circular vibration and an infinity of circular elements vibrating in the same sense. Kinematic integration gives a single circular vibration in this sense. This consideration, therefore, leads to the same result as the assumption, made above, of direct penetration of the pencil as a whole, and subsequent reflexion at a definite depth. The two resulting opposite circular vibrations now possess difference of phase, thence rotation, and slight difference of amplitude, thence slight ellipticity in the reflected ray. (Compare the geometrical method of circular elements by Dr. Wiener, *Wied. Ann.* xxxv. pp. 3-5, 1888.)

† Voigt, *Wied. Ann.* xxiii. p. 508 (1884).

XXVIII. *On the Acceleration of Secondary Electromagnetic Waves.* By FRED. T. TROUTON*.

[Plate VI.]

IT is well known that if, after the manner of Huygens's construction, the effect of a wave-surface at any point be determined by summing up the individual effects of the secondary waves obtained, by supposing the surface divided up into elementary portions, each element of surface acting as an independent source, it becomes necessary to assume that an elementary portion produces its effect at the point with an acceleration of phase of $\frac{1}{4}$ period in advance of the effect produced at the point by the general wave-surface, otherwise the sum of the secondary effects would possess a phase $\frac{1}{4}$ period in error.

As ordinarily considered †, it is somewhat surprising that there should be this change of phase in a wave coming from an element of surface. But the consideration of this question, in the light of Hertz's investigations on the radiation emitted from an electromagnetic "vibrator" or discharging condenser, seems to be particularly suggestive.

At first the magnetic component of the wave will be taken, as it can be more simply dealt with. Considering, for the moment, points situated along a line at right angles to, and starting from, the centre of a "vibrator," Hertz's expression ‡ for the magnetic component of the electromagnetic wave at a distance r is

$$P = \frac{a}{r} \left\{ \sin 2\pi \left(\frac{r}{\lambda} - \frac{t}{\tau} \right) + \frac{\lambda}{2\pi r} \cos 2\pi \left(\frac{r}{\lambda} - \frac{t}{\tau} \right) \right\}.$$

At points near the "vibrator" the vibration is easily seen to depend almost entirely on the latter term, or

$$P = \frac{a\lambda}{2\pi r} \cos 2\pi \left(\frac{r}{\lambda} - \frac{t}{\tau} \right);$$

while at a distance it depends in like manner on the first term, or, as it may be written,

$$P = \frac{a}{r} \cos 2\pi \left\{ \frac{r}{\lambda} - \left(\frac{t}{\tau} + \frac{1}{4} \right) \right\}.$$

* Communicated by the Author.

† The complete Elastic Solid Theory contains this acceleration. See *Enc. Brit.*, art. "Wave Motion," p. 453.

‡ Wiedemann's *Annalen*, January 1889; also 'Nature,' February 21, 1889.

This at once points to an acceleration of phase of $\frac{1}{4}$ period at distances remote from the "vibrator."

The rate at which the magnetic component of the disturbance is propagated can be determined by taking a definite position on the wave and finding how r varies with respect to t on travelling out with the wave in this phase. If $P=0$, then

$$\tan (mr - nt) = -1/mr.$$

Here m stands for $2\pi/\lambda$, and n for $2\pi/\tau$. From this we get for the velocity of the wave,

$$v = \frac{dr}{dt} = V \frac{m^2 r^2 + 1}{m^2 r^2},$$

where V is the normal velocity, or that at a great distance from the "vibrator." When $r=0$, v has an infinite value, but on going outwards rapidly approximates to V . Hertz has pointed out that the true interpretation of this great value for the velocity at points near the origin involves the idea of the energy radiated really coming from points in the surrounding medium, the true seat of the oscillations.

Thus, from the consideration of velocity an acceleration in phase is observed to occur. To find its amount, the time the disturbance takes to reach a point at distance $N\lambda$ from the origin can be easily found and compared with the normal time. Thus

$$\int_0^{N\lambda} \frac{dr}{v} = \frac{1}{V} \left\{ N\lambda + \frac{\lambda}{2\pi} \tan^{-1} \frac{1}{2\pi N} - \frac{\lambda}{4} \right\}.$$

When N is a large number this approximates to the value $N\tau - \tau/4$, and is an acceleration corresponding to one quarter period.

If the position of maximum or minimum value of P (i.e. $\frac{dP}{dr} = 0$ *) be taken on the wave instead of the zero value,

we shall have $\tan (mr - nt) = mr$, and the same expression for the velocity is found. The circular electric-line of force in Hertz's diagrams of the disturbance, here reproduced for convenience of reference, also spreads out with this velocity.

* It is to be particularly observed that in the neighbourhood of the conductor, unlike in normal wave motion, the position on the wave where $\frac{dP}{dr} = 0$ is not the position on the wave of maximum displacement; this state of the wave will be found like the electric force to originate at $\lambda/4$, having a very similar expression for the rate of its propagation. On plotting the curve P at a series of stated epochs this is well shown.

The electric component of the wave*

$$z = \frac{a}{r} \left\{ -\sin (mr - nt) - \frac{\cos (mr - nt)}{mr} + \frac{\sin (mr - nt)}{m^2 r^2} \right\}$$

may in like manner be considered. Similarly to before, if $z=0$, it is necessary everywhere along the line considered that

$$\tan (mr - nt) = \frac{mr}{1 - m^2 r^2}$$

From this we get for the velocity,

$$v = V \frac{m^4 r^4 - m^2 r^2 + 1}{m^2 r^2 (m^2 r^2 - 2)}.$$

In this case v has an infinite value both at the centre and at distance $\lambda/\pi\sqrt{2}$ —roughly $\lambda/4.4$. At intermediate points it is negative or towards the centre. As the wave passes outwards it is at this point $\lambda/4.4$ that the zero value of z is first reached (at about $.12\tau$ before it becomes zero at the centre, which occurs at $\tau/2$), whence it spreads both outwards and inwards. On the diagrams this appearance of the zero value of z is easily traced, and its subsequent outward movement at the centre of the small circles; these of course are the cross sections of a vortex-ring, as it were, thrown off by the “vibrator.”

For determining the time to reach any point, we have

$$\int \frac{dr}{v} = \frac{1}{V} \left\{ r - \frac{1}{m} \tan^{-1} \frac{mr}{1 - m^2 r^2} + \text{const.} \right\}.$$

This between $N\lambda$ and $\lambda/4.4$, when N is a large number, gives as the time taken,

$$\tau(N - 1/4.4) - \tau/2\pi \cdot \tan^{-1} \sqrt{2},$$

the first part being the normal time.

If we wish from this to determine the period elapsing between the arrival of the wave in this phase at the point $N\lambda$ and the time of zero value of the electric force at the centre which occurs at the epoch of fig. 1, Plate VI., we must add the epoch of the appearance at $\lambda/4.4$. This will be found to afford NT , the normal time. But if we reckon from the time the zero value, having appeared at $\lambda/4.4$, travelling inwards reaches the centre, we obtain $NT - \tau/2$, an acceleration of one half-period. In neither case, it is to be observed, does it represent the time of passage between two places. The zero value of z at the centre in fig. 1 ought really to be referred

* Wiedemann's *Annalen* for 1889.

to the previous swing. This will be better understood by recollecting that *at* the conductor, when the electric force is at its greatest development, the current is zero, and consequently so, too, the magnetic force, while in radiation the electric force and the magnetic force simultaneously reach their maximum value. This is beautifully shown in Hertz's diagrams. In fig. 1, at the centre the electric force is zero, while the magnetic force is about at its greatest development. The latter travels outwards with such a velocity at each point (the same as that of the circular line of force in the diagrams) that there is an acceleration of $\frac{1}{4}$ period; while the former vanishes at the centre but reappears at $\lambda/4$, as is seen in fig. 4, so as to be now one quarter wave-length behind. In this way the necessary readjustment of the relative phases of the electric and magnetic components is effected.

If the position on the wave of maximum or minimum value of z (that is to say, the "crest") be taken instead of the zero value, the condition at any point is that

$$\tan (mr - nt) = \frac{m^2 r^2 - 1}{mr},$$

and the same expression for the velocity as before is obtained, so that the position at distance $\lambda/4$ may be considered the point from which the electric disturbance originates, and not the centre. As the energy in the neighbourhood of the conductor turns from its magnetic to its electric form*, it is at this point that the maximum value is first reached, and is in advance of the "normal epoch" $\tau/4$, or that of the "crest" at the centre by about $\frac{1}{8}\tau$. The maximum value spreads both outwards and inwards from $\lambda/4$, reaching the centre at $\tau/4$, the epoch of fig. 3.

As in the case of the zero value of z , so here also, if the period elapsing between the arrival at any point and the time of greatest electric development at the centre, which occurs at the epoch of fig. 3, be calculated, an acceleration of $\tau/2$ on the normal time is found. This virtual acceleration of $\tau/2$ is, however, due to the combined effect of the "crest" or maximum value of z , (1) starting from the point $\lambda/4$ instead of from the centre, (2) at a time about $\frac{1}{8}\tau$ previous to the normal epoch $\tau/4$ or that at the centre, (3) as well as to the

* In the curves obtained by plotting z for a series of epochs the formation of the wave at $\lambda/4$ is clearly observed. The wave after springing here into existence above the zero-line, lengthens out in both directions, and then beginning to sag in the centre, finally splits into two at this point, as the force reaches zero, again to pass over to the other side of the zero-line.

increased velocity. As mentioned before, the acceleration of the rate of propagation of the electric component of the disturbance must differ by $\pi/4$ from that of the magnetic component in order to provide the necessary readjustment of their relative phases.

The question now arises if, on the whole, the elementary disturbance to be supposed in Huygens' construction* may not fairly be considered as being of the same character as that produced by a Hertzian "vibrator." Such an elementary disturbance as is there assumed, in the absence of neighbouring ones, would have apparently uncompensated ends or poles equivalent to the opposite electrifications on a "vibrator." Of course the only way we know of producing an elementary disturbance is by the presence of matter, so that it seems natural to take the disturbance assumed in Huygens' construction to be similar in its effects. It might perhaps be objected to this that a "vibrator" is a conductor, and that there are conduction-currents to be dealt with; but as against this the fact is to be considered that, as we shall see, a non-conductor such as glass can act by reflexion so as to be the source of such an elementary disturbance.

Some experiments were described in 'Nature' (August 22, 1889) in which this acceleration in phase was actually observed to take place in the reflexion from a small surface. It was there described how, in Hertz's experiment of "loop and nodes," if a *small* sized reflector be employed, the magnetic node, instead of being at $\frac{1}{4}\lambda$ from the reflector, is found to be nearly $\frac{1}{8}\lambda$ further out. This evidently corresponds to a change of phase of $\frac{1}{4}$ period in the reflected wave, for the distance $\frac{1}{8}\lambda$ has to be twice traversed.

The way in which this change in phase is brought about is perhaps most conveniently considered by supposing the small reflector to be itself resonant, or equivalent to a second vibrator having the requisite phase with reference to the incident wave. And indeed that something such as this occurs may even be noticed by touching the mirror with a small piece of metal; for bright sparks can be drawn from the two edges running at right angles to the electric force, while little or no effect is obtained from the central parts.

Let the magnetic component of the wave incident vertically on the reflector, and supposed a parallel beam, be taken as

$$P = A \cos 2\pi \left(\frac{t}{\tau} + \frac{r}{\lambda} \right);$$

* In the case of sound, the divergency of the direction of motion of the particles from an element of surface affords the analogous reason for the acceleration.

where r is the distance to the reflector, and A is the amplitude of the magnetic force. The magnetic component of the reflected wave, supposed as above to be from a second "vibrator," will be given by *

$$P' = \frac{4\pi^2 El}{\lambda^2 r} \left\{ \sin 2\pi \left(\frac{r'}{\lambda} - \frac{t}{\tau} \right) + \frac{\lambda}{2\pi r} \cos 2\pi \left(\frac{r}{\lambda} - \frac{t}{\tau} \right) \right\},$$

as this has the same phase at the reflector as the incident beam. Here $\pm E$ is the maximum value of the electrification induced by the incident wave on the second "vibrator," and l is the equivalent distance apart of the positive and negative charges, which, taken roughly, is the length in the direction of the electric displacement of the reflector supposed rectangular. An approximation for E may be easily obtained from the value for the induced current arrived at, by assuming that the magnetic force parallel to the reflector due to the induced current is such as to neutralize the effect of the direct radiation immediately behind the reflector†. If c is the amount of the current per centimetre cross section in the reflector, the magnetic force due thereto parallel to the reflector and close up to it is $2\pi c$; that is to say, it is assumed equal to the force due to an infinite current-sheet of intensity c per centimetre cross section. (See Maxwell, chap. xii.) This is to be put equal to the magnetic force of the direct radiation at the reflector $A \cos 2\pi \frac{t}{\tau}$. Recollecting that c is in electromagnetic units, we have for the amplitude of the total charge along the edge k of the reflector,

$$E = kV \int_0^{\tau/4} c \, dt = kV \int_0^{\tau/4} \frac{A}{2\pi} \cos 2\pi \frac{t}{\tau} \, dt = \frac{Ak\lambda}{4\pi^2}.$$

This neglects the end irregularities in the electrification.

At any point in front of the reflector the disturbance is the sum of P and P' , and we have a series of stationary waves, complicated, however, by the fact that the velocity and the amplitude of one of the components are functions of the distance.

$$P + P' = B \cos 2\pi \left(\frac{t}{\tau} + \alpha \right)$$

represents the stationary waves when

$$B^2 = A^2 \left\{ 1 + 2 \cdot \frac{kl}{r\lambda} \left(\sin 4\pi \frac{r}{\lambda} + \frac{\lambda}{2\pi r} \cos 4\pi \frac{r}{\lambda} \right) + \left(\frac{kl}{r\lambda} \right)^2 \left[1 + \left(\frac{\lambda}{2\pi r} \right)^2 \right] \right\}.$$

* Wiedemann's *Annalen*, January 1889.

† This, as a method of evaluating the electrification, was pointed out to the author by Prof. Fitzgerald.

Practically the quickest method for determining the positions of maxima and minima for B is to plot the curve represented by this equation in each particular case. The curve shown in fig. 5, Pl. VI. is that where $k=30c$, $l=22c$, and $\lambda=72c$. The abscissa represents the distance, measured in centimetres, from the reflector to the point, while the ordinate multiplied by A^2 represents the intensity or square of the amplitude of the magnetic force of the stationary wave at the point. The dotted line indicates the intensity of the direct radiation, to which the curve is seen to approximate as r increases in value. The curve is seen to be going off the limits of the paper on the side next the reflector; but it must be remembered that in this region the formulæ used have but an indirect interpretation as the finite size of the reflector becomes important, and that there is involved the idea of the æther here being in special commotion, so that reflexion may in a certain sense be looked upon as taking place before really reaching the mirror.

On examining the curve the first minimum will be seen to occur at about $24c$ from the reflector, which agrees sufficiently well for an approximate method of calculation with the result of experiment, which for a wave-length of $72c$ gives the first minimum at about $25c$.* And in fact we might expect, on looking at the curve, that the experiment as made would always tend to give the minimum a little beyond its true position; for if the spark-gap be set to just observe a spark of, say, the direct waves' intensity, and if the distance be bisected between the positions to right and left of the minimum where sparking is observed to commence on moving along the "receiver," this point will be too far out, owing to the portion of the curve to the left being steeper than that to the right. This is well marked when working with the spark-gap comparatively open; that is to say, various positions are then obtained for the minimum according to the width of the spark-gap. This was experimentally noticed before the curve was plotted.

The curve indicates at once the reason why it is difficult to

* In this Table the results of experiments with different wave-lengths are shown in the third column.

λ .	$\frac{2}{3}\lambda$.	Min.
72	27	25
68	25.5	24
60	22.5	21
56	21	19

observe even the second minimum. It will also be noticed from the curve that the second minimum is at a distance from the first slightly greater than the half wave-length ; so that if the curve were continued further out we might very well expect the minima to be shifted out the complete $\frac{1}{2}\lambda$, as in fact may be seen to be the case from the equation of the curve. This in ordinary wave theory would be referred to the necessity for the point to be at a proportionate distance before a given surface can be considered as truly sending out a *secondary* wave. Some experiments were made which certainly tended towards showing that this lengthening of the distance between the first and second minimum exists ; but the experiments were unsatisfactory, for the second minimum is very slightly marked, and experimentally indeed seems to be even less so than one would expect from the curve. However, it is most likely that the Hertzian stationary waves are never so well marked as they would ordinarily be calculated ; for it seems most probable that primary “vibrators” do not send out strictly “monochromatic light,” but send out a number of wave-lengths of nearly the same period—a “band-spectrum,” so to speak, the centre of which no doubt may be by far the strongest, and correspond with the “period” as would be calculated for the “vibrator ;” also that “secondary vibrators” or resonators may in like manner be forced so as to take up, in some degree depending on the discrepancy, any member of a “band-spectrum” special to each resonator, its “period” corresponding to the centre*. Thus the marking of a node belonging to the central wave-length will probably be weakened, owing to the presence of the other members of the “band” whose nodes on the whole will occur elsewhere.

An observation which has proved of use in the course of these experiments on secondary waves was made during the autumn, namely that glass absorbed Hertzian radiations comparatively rapidly ; in fact on account of this property it was found quite impracticable to determine the velocity of “light” in glass by the method† of interposing a sheet of the substance in front of a reflector affording stationary waves, because the front surface of the glass itself gave a well-marked series of loops and nodes. A comparatively thin piece of glass, say of one centimetre, will afford an observable reflexion. This must be due chiefly to the reflexion from the second surface being weakened by absorption, so that it is insufficient to

* The author hopes shortly to publish an account of experiments made during the autumn which have led to these conclusions.

† ‘Nature,’ August 22, 1889.

seriously interfere with that from the front, but also no doubt to reflexions from points situated in the substance of the glass. A sheet of glass two centimetres thick gives fairly good reflexion, while a sheet of paraffin of that thickness would give almost no effect.

Thus by using glass it was comparatively easy to obtain stationary waves by reflexion from a small surface of a non-conducting substance, in order to compare the effect thus produced on the position of the stationary waves with that produced by employing a small metallic reflector. The first node was found to be shifted out nearly $\frac{1}{8}\lambda$, as in the case of metallic reflexion. That reflexion from glass is not of the metallic sort was proved by obtaining polarized reflexion. In this case the two opposite edges of the nonconductor may be looked upon as undergoing variations of apparent electrification.

XXIX. *On the Time-integral of a Transient Electromagnetically Induced Current.* By Sir WILLIAM THOMSON, F.R.S.*

IT has hitherto been generally supposed that, in ordinary apparatus for electromagnetic induction, with or without soft iron, the oppositely directed transient currents, in the secondary circuit, induced by startings and stoppings of current in the primary circuit, have equal time-integrals.

I have recently perceived [been wrongly led to imagine] that this may be far from being practically the case by the following considerations. The starting and stopping of the current in the primary circuit was, in Faraday's original discovery of this kind of electromagnetic-induction (Exp. Res. Series I. Nov. 1831), and is generally in elementary illustrative experiments, produced by making and breaking a circuit consisting of a voltaic element or battery and the inductor-wire. In this arrangement the starting of the inductor-current is generally much less sudden than the stopping. Hence a thicker shell of the secondary wire (or portion inwards from the outward boundary) is utilized for conducting the secondary current, on the make, than on the break†. Hence the effective ohmic resistance in

* Communicated by the Author.

† [In reality the whole cross sectional area of the secondary conductor is utilized, equally in all its parts, in conducting the secondary current. See Postscript of February 23.]

the secondary circuit is less to the current induced by the make than to the current induced by the break; and the time-integral of the former current is correspondingly greater than the time-integral of the latter.

Faraday in his first experiment found the current induced by the make to be greater than that induced by the break, but he explained it by the running down of his voltaic battery during the time the current was passing through the primary, in consequence of which the magnitude of the current stopped on the break was smaller than that of the current instituted on the make. This was undoubtedly a *vera causa*, and probably one of considerable potency, considering that Faraday had then no Daniel's battery and had no storage-cells to serve him in his work. Another *vera causa* is the heating of the circuit, which, even with a battery of constant E.M.F., may render the current started very considerably greater than the current stopped in ordinary experiments. Faraday, in his original experiments*, had only magnetization of steel wires to discover the induced currents by, and to test their magnitude; and he had no galvanometer in the primary circuit. If he had had a ballistic galvanometer in his secondary circuit, and any suitable galvanometer for steady currents in his primary circuit, he might possibly have found† that the time-integral (as shown by the ballistic galvanometer) of the primary current exceeded that of the secondary current by a greater difference than could be accounted for by the current being suddenly started and the current suddenly stopped in the primary. So far as I know no one, from 1831 till now, has made any experimental examination of the question suggested in Faraday's Exp. Res. Series I. 16; and his idea that the two currents are equal has been generally accepted‡. I have therefore asked Mr. Tanakadaté to make some experiments on the subject in my laboratory. He immediately obtained results§ seeming to demonstrate a con-

* Exp. Researches, Series I., 1831.

† [No. On the contrary, he would have found that his first idea, of perfect equality of the two currents, was perfectly true! February 23.]

‡ See Maxwell's 'Electricity and Magnetism' (1873), vol. ii. §537, p. 171.

§ But these results we find are quite untrustworthy because of the susceptibility of the steel needle of the galvanometer to magnetic induction, which with the currents produced through its coil by the induced currents due to the make and break in the primary circuit, may *largely alter its effective magnetism*. It is in fact well known that ballistic galvanometers with steel needles give very erratic results if they are used in attempting to find time-integrals of very intense transient currents of very short duration.

siderable excess in the time-integral (as shown by a ballistic galvanometer) of the secondary current on the make above that on the break. A magneto-static galvanometer in the primary circuit showed the current before the break to be always a little less than immediately after the make. This difference was due to heating of the primary circuit, because a potential galvanometer applied to the two terminals of the voltaic element used, which was a large storage-cell, showed no sensible drop of potential during the flow of the current in the primary circuit. It was, however, insufficient to account for the large differences found between the ballistic deflexions produced by the induced currents on the make and on the break. A rapid succession of makes and breaks has given large irregular permanent deflexions of the ballistic galvanometer, sometimes in one direction, sometimes in the other, which we have found to be chiefly due to magnetic susceptibility of the steel needle of the ballistic galvanometer: and we find that this cause has probably vitiated the observations on the effects of single makes and breaks. I have therefore arranged to have experiments continued, with a coil of very fine wire bifilarly suspended, instead of the steel needle of the ballistic galvanometer; a steady current through the fine wire being maintained by an independent voltaic battery.

Hitherto the make and break have been performed by hand, dipping a wire into and lifting it out of a cup of mercury.

Various well-known methods may be used to render either the break or the make so gradual that we may be sure of the induced current running practically *full-bore* through the secondary. On the other hand, very sudden breaks may be effected by separating two little balls or other convex pieces of copper by the blow of a hammer. The experiment may be varied by short-circuiting the ends of the inductor and allowing the current from the battery to continue flowing through electrodes of sufficient resistance not to allow an injuriously great amount of current to flow. These electrodes, between the voltaic element and the ends of the inductor-wire, may have large self-inductance given to them by coiling them round a closed magnetic circuit of soft iron. The starting of the current in the inductor-wire will thus be rendered much more sudden than the stopping; and the induced current in the secondary will no doubt be found stronger on the stoppage than on the start. Mr. Tanakadaté is continuing the experiments with these modifications in view.

The mathematical foundation of the common opinion that

the time-integrals of the induced currents on the make and break are equal is as follows*.

Let β and γ be the currents at time t in the primary and in the secondary circuits respectively; J the self-inductance of the secondary circuit; and M the mutual inductance of the two. We have

$$R\gamma = -M \frac{d\beta}{dt} - J \frac{d\gamma}{dt}.$$

Hence if $\gamma=0$ when $t=0$, and if we suppose R to be constant,

$$\int_0^t \gamma dt = \frac{M}{R} (\beta_0 - \beta) - \frac{J}{R} \gamma.$$

Now let T be any value of t so large that β has become sensibly constant, and γ has subsided to zero. We have

$$\int_0^T \gamma dt = \frac{M}{R} (\beta_0 - \beta_T).$$

This shows that the time-integral of the induced current in the secondary circuit would depend solely on the difference of values of the current in the primary at the beginning and end of the time included in the reckoning, and would be quite

[* February 23.—Worked out more perfectly it shows, as follows, that the common opinion is correct!

Imagine the whole secondary conductor divided into infinitely small filaments of cross-section $d\Omega$: and let ξ be the current-density, at time t , in any one of these. Instead of γ in the text take $\xi d\Omega$, and instead of R take $l(\sigma d\Omega)$; σ denoting the specific conductivity of the material, and l the length of the circuit. We have

$$l\sigma^{-1}\xi = -M \frac{d\beta}{dt} - J \frac{d\xi d\Omega}{dt} - S,$$

where S denotes the sum of effects due to the risings and fallings of current in the different parts of the secondary conductor. Their time-integral from 0 to T is essentially zero; as is also that of the infinitesimal middle term of the second member. Hence we have

$$l\sigma^{-1} \int_0^T dt \xi = M(\beta - \beta_0);$$

which shows that the time-integral of the current, $\xi d\Omega$, in each filament of the secondary conductor, is exactly equal to that which is calculated according to the ordinary elementary theory! The whole details of the fallacy in the text are now clear!]

independent of suddennesses, *if the effective ohmic resistance were constant*. But this supposition is not true; and that it is very effectively untrue for copper wires of a millim. diameter or more, and times of change in the primary less than $\frac{1}{300}$ of a second, we see readily by looking to the diffusional curve and the time-number, $\frac{1}{20}$ of a second for curve 10, corresponding to the diffusivity of copper for electric currents (which is 131 square centimetres per second) given and explained in my short article on a Five-fold Analogy, in the British Association Report for Manchester, 1888 (to be found also in the Electrical Journals, and 'Nature').

[POSTSCRIPT, *February 23, 1890.*—The thermal analogy, which is very simple for the case of electric currents in parallel straight lines, has, as soon as I have considered it, shown me the fallacy pervading the text; and has led me to make the corrections in the insertion and footnotes enclosed in brackets [], all of which are of the date of this postscript. Preliminary experiments with the suspended coil instead of the steel magnet, in a ballistic galvanometer now nearly completed by Mr. Tanakadaté, have already disproved the *large* differences which I expected between the time-integrals of the secondary currents on the break, and on the make; and as far as they have yet gone are consistent with the *perfect equality* which I now find proved by theory.]

XXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 135.]

December 18, 1889.—W. T. Blanford, LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. "On the Occurrence of the Genus *Girvanella*, and remarks on the Oolitic Structure." By E. Wethered, Esq., F.G.S.

2. "On the Relation of the Westleton Beds or 'Pebbly Sands' of Suffolk to those of Norfolk, and on their extension inland, with some observations on the Period of the final Elevation and Denudation of the Weald and of the Thames Valley."—Part II. By Prof. Joseph Prestwich, M.A., D.C.L., F.R.S., F.G.S.

The author having, in the first part of this paper*, discussed the relationship of the Westleton Beds to the Crag Series and to

* Phil. Mag. [5] xxviii. p. 142.

the Glacial Deposits, proceeded in the present contribution to consider the extension of the Westleton Beds beyond the area of the Crag, and described their range inland through Suffolk, East, West, and South Essex, Middlesex, North and South Hertfordshire, South Buckinghamshire, and North and South Berkshire, noticing their relationship to the overlying Glacial beds, where these were developed, and the manner in which they reposed upon older deposits. He gave an account of the heights of the various exposures above Ordnance Datum, and mentioned the relative proportion of the different constituents in various sections, thus showing that in their southerly and westerly extension they differed both in composition and in mode of distribution from the Glacial deposits. Distinction was also made between the Westleton Beds and the Brentwood Beds.

Attention was next directed to the occurrence of the Westleton Series, south of the Thames, in Kent, Surrey, and Hampshire, and their possible extension into Somersetshire was inferred from the character of the deposits on Kingsdown and near Clevedon.

In tracing the deposits from the east coast to the Berkshire Downs it was noticed that at the former place the beds lay at sea-level, but ranging inland, they gradually rose to heights of from 500 to 600 feet: that in the first instance they underlay all the Glacial deposits, and in the second they rose high above them, and their seeming subordination to the Glacial series altogether disappeared: thus at Braintree, where the Westleton Beds were largely developed, they stood up through the Boulder-clay and gravel which wrapped round their base, whilst further west, where they became diminished to mere shingle-beds, they attained heights of from 350 to 400 feet, capping London-clay hills, where the Boulder-clay lay from 80 to 100 feet lower down the slopes, the difference of level between the two deposits becoming still greater in a westerly direction, until finally the Boulder-clay disappeared.

The origin of the component pebbles of the beds was discussed, and their derivation traced (1) to the beds of Woolwich age in Kent, N. France and Belgium, and possibly to some Diestian beds, (2) to the older rocks of the Ardennes, (3) to the Chalk and older drifts, and (4) to the Lower Greensand of Kent and Surrey, or in part to the Southern drift.

The marine nature of the beds was inferred from the included fossils of the type-area, and the absence of these elsewhere accounted for by decalcification.

The southward extension of the beds was shown to be limited by the anticlinal of the Ardennes and the Weald, and the scanty palæontological evidence of the nature of that land was noted, and the possible existence of the Scandinavian ice-sheet to the north was referred to in connexion with the disappearance of the beds in that direction.

From the uniform character of the Westleton shingles the author *Phil. Mag.* S. 5. Vol. 29. No. 178. *March* 1890. Y

maintained that they must originally have been formed on a comparatively level sea-floor, and that the inequalities in distribution had been produced by subsequent differential movement to the extent of 500 feet or more to the north and west above that experienced to the east and south, where the chronological succession remained unbroken, also that the inequalities below the level of the Westleton beds had been produced since the period of their deposition, as, for instance, the gorge of the Thames at Pangbourne and Goring, and most of the Preglacial valleys in the district; furthermore, evidence was adduced in favour of the formation of the escarpments of the Chalk and Oolites since Westleton times, whilst certain observations supplied data for estimation of the relative amounts of pre- and post-glacial denudation of the valleys.

It was stated, in conclusion, that the time for the vast amount of denudation was so limited that it was not easy to realize that such limits could suffice, but the author did not see how the conclusions which he had arrived at could well be avoided.

January 8, 1890.—W. T. Blanford, LL.D., F.R.S., President,
in the Chair.

The following communications were read:—

1. "On some British Jurassic Fish-remains referable to the genera *Eurycormus* and *Hypsocormus*." By A. Smith Woodward, Esq., F.G.S.

2. "On the Pebidian Volcanic Series of St. Davids." By Prof. C. Lloyd Morgan, F.G.S.

After a brief sketch of the principal theories that have been propounded, the author concluded that our knowledge of this series has not yet reached "a satisfactory position of stable equilibrium." His own communication was divided into three sections.

The Relation of Pebidian to Cambrian.—There are four localities where the junction is described—Caerbwdy Valley, St. Non's Bay, Ogof Golchfa, and Ramsey Sound. The stratigraphy of the second of these was given with much detail, and illustrated. The author concluded that here, together with clear signs of local or contemporaneous erosion, the general parallelism of the strike of Pebidian and Cambrian is most marked. There is no evidence of any bending round of the conglomerate against the strike of the Pebidians. The stratigraphical evidence in each of the localities having been considered, together with the evidence offered by the materials of the Cambrian conglomerate and local interstratification with the volcanic beds (the interdigitation at Carnarwig being well marked), he concluded that there was no great break between the conglomerate and the underlying Pebidians. The uppermost Pebidian already foreshadowed the sedimentary conditions of the Harlech strata, and the

change emphasized by the conglomerate was one that followed volcanic conditions after no great lapse of time.

Hence the relation of the Pebidian to the Cambrian is that of a volcanic series, for the most part submarine, to succeeding sedimentary strata—these strata being introduced by a conglomerate formed in the main of foreign pebbles borne onward by a current which swept the surface of, and eroded channels in, the volcanic tuffs and other deposits. He was disposed to retain the name Pebidian as a volcanic series in the base of the Cambrian system.

The Pebidian Succession.—With the exception of some cinder-beds, which appear to be subaerial, the whole series was accumulated under water. There is no justification for making separate subdivisions; the series consists of alternating beds of tuff of varying colour and basicity, the prevailing tints being dark green, red-grey, and light sea-green. In the upper beds there is an increasing amount of sedimentary material, and more rounded pebbles are found. Basic lava-flows occur, for the most part, in the upper beds. Detailed work, laid down on the 6-inch Ordnance map, appears to establish a series of three folds—a northern anticline, a central syncline, and a southern anticline—folded over to form an isocline, with reversed dips to the S.E. The axis of folding is roughly parallel to the axis of St. David's promontory. The total thickness is from 1200 to 1500 ft.

The author devoted a considerable number of pages to further details concerning this series of deposits. He failed to find the alleged Cambrian overlap. "The probabilities are that it is by step-faults between Rhoson and Porth Sele, and not by overlap, that the displacement of the conglomerate has there been effected." Also at Ogof Gôch it does not rest upon the quartz-felsite breccia and sheets (group C, of Dr. Hicks), but is faulted against them. A section was devoted to the felsitic dykes, and it was suggested that they may be volcanic dykes of Cambrian age.

The Relation of the Pebidian to the Dimetian.—The author has not been able to satisfy himself of the existence of the Arvonian as a separate and distinct system. He notes the junction of Pebidian and Dimetian in Porthlisky Bay and the Allen Valley at Porth Clais, at neither of which places are there satisfactory evidences of intrusion. At Ogof Llesugn the intrusive character of the Dimetian was strongly impressed upon him. He criticised the mapping of Dr. Hicks, and pointed out the difficulties which present themselves in the way of mapping the Dimetian ridge as Pre-Cambrian. He pointed out that not a single pebble of Dimetian rock, such as those now lying on the beach in Porthlisky Bay, is to be found in the conglomerate. He concluded that the Dimetian is intrusive in the southern limb of the isocline, and that there are no Archæan rocks *in situ*.

January 22.—W. T. Blanford, I.L.D., F.R.S., President,
in the Chair.

The following communication was read:—

“On the Crystalline Schists and their relation to the Mesozoic Rocks in the Lepontine Alps.” By Professor T. G. Bonney, D.Sc., I.L.D., F.R.S., F.G.S.

In the debate upon the paper “On two Traverses of the Crystalline Rocks of the Alps” (read Dec. 5, 1888) it was stated that rocks had been asserted on good authority to exist in the Lepontine Alps, which contained Mesozoic fossils, together with garnets, staurolites, &c., and thus were undistinguishable from crystalline schists regarded by the author as belonging to the presumably Archæan *massifs* of that mountain-chain. In reply, the author stated that he regarded this as a challenge to demonstrate the soundness or unsoundness of the hypothesis to which he had committed himself. The present paper gives the result of his investigations, undertaken in the month of July, 1889, in company with Mr. James Eccles, F.G.S., to whom the author is deeply indebted for invaluable help. The paper deals with the following subjects:—

(1) *The Andermatt Section.*

By the geologists aforesaid, a highly crystalline white marble which occurs on the northern side of the Urserenthal trough, at and above Altkirch, near Andermatt, is referred to the Jurassic series (members of which undoubtedly occur at no great distance, almost on the same line of strike). The author describes the relation of the marble to an adjacent black schistose slate, and discusses the significance of some markings in the former which might readily be considered as organic, but to which he assigns to a different origin. He shows that there are most serious difficulties in regarding these two rocks as members of the same series, and explains the apparent sequence as the result of a sharp and probably broken infold, as in the case of the admitted band of Carboniferous rock at Andermatt itself. That the section is a difficult one on any hypothesis the author admits, but in regard to the former of these, after a discussion of the evidence, he concludes “that tendered on the spot demands a verdict of ‘not proven’—that obtainable in other parts of the Alps will compel us to add, ‘not provable.’”

(2) *The Schists of the Val Piora.*

These schists, already noticed by the author in his Presidential Address to the Society in 1886, occur in force near the Lago di Ritom, and consist of two groups:—the one, dark mica-schists, sometimes containing conspicuous black garnets, banded with quartzites, the other, various calc-mica schists; between them, apparently not very persistent, occurs a schist containing rather large staurolites or kyanites. On the north side is a prolongation of the garnet-actino-

lite (Tremola-) schists of the St. Gothard and then gneiss; on the south side gneiss. There is also some rauchwacké. This rock, at first sight, appears to underlie the Piora-schists, and thus to be the lowest member of a trough. If so, as it is admittedly about Triassic in age, the Piora-schists would be Mesozoic. The author shows that (1) the latter rocks do not form a simple fold; (2) they are beyond all question altered sediments; (3) they have often been greatly crushed subsequent to mineralization; (4) the garnets, staurolites, &c. (if not injured by subsequent crushing) are well developed and characteristic, and are authigenous minerals.

(3) *The Rauchwacké and its Relation to the Schist.*

(a) *The Val-Piora Sections.*—The author shows that the rauchwacké, which at first sight seems to underlie the dark mica-schist, is inconstant in position (on the assumption of a stratigraphical sequence); that its crystalline condition does not resemble that of the schist-series, but is rather such as is common in a rock of its age; that it contains mica and other minerals of derivative origin, and in places rock-fragments which precisely resemble members of the Piora-schist series.

(b) *The Val-Canaria Section.*—This section, described by Dr. Grubenmann, is discussed at length. It is shown that the idea of a simple trough is not tenable, for identical schists occur above and below the rauchwacké; that there is evidence of great pressure, which, however, acted subsequently to the mineralization of the schists; and that in one place the rauchwacké is full of fragments of the very schists which are supposed to overlie it.

(c) *Nufenen Pass &c.*—Other cases, further to the west, are described, where confirmatory evidence is obtained as to great difference in age between the rauchwacké and the schists, and the antiquity of the latter. The apparent interstratification is explained by thrust-faulting,

(4) *The Jurassic Rocks, containing Fossils and Minerals.*

The author describes the sections on the Alp Vitgira, Scopi, and the Nufenen Pass. Here indubitable Belemnites and fragments of Crinoids occur in a dark, schistose, somewhat micaceous rock, which is often very full of “knots” and “prisms” of rather ill-defined external form, something like rounded garnets and ill-developed staurolites. These rocks at the Alp Vitgira appear to overlie, and in the field can be distinguished from the black-garnet schists. In one place the rock resembles a compressed breccia, and among the constituent fragments is a rock very like a crushed variety of the black-garnet mica-schist. These Jurassic “schists” are totally different from the last-named schists, to which they often present considerable superficial resemblance; for instance, their matrix is highly calcareous, the other rock mainly consisting of silicates.

Some of the associated mica may be authigenous, but the author believes much of it and other small constituents to be derivative. There is, however, a mineral resembling a mica, exhibiting twinning with (?) simultaneous extinction, which is authigenous. The knots are merely matrix clotted together by some undefinable silicate, and under the microscope have no resemblance to the "black garnets." The prisms are much the same, but slightly better defined; they present no resemblance to the staurolites, but may be couseranite, or a mineral allied to dipyre. Hence, though there is rather more alteration in these rocks than is usual with members of the Mesozoic series, and an interesting group of minerals is produced, these so-called schists differ about as widely as possible from the crystalline schists of the Alps, and do not affect the arguments in favour of the antiquity of the latter. In short, they may be compared to rather poor forgeries of genuine antiques. Incidentally the author's observations indicate (as he has already noticed) that a cleavage-foliation had been produced in some of the Alpine schists anterior to Triassic times.

February 5.—W. T. Blanford, LL.D., F.R.S., President,
in the Chair.

The following communications were read:—

1. "The Variolitic Rocks of Mont-Genèvre." By Grenville A. J. Cole, Esq., F.G.S., and J. W. Gregory, Esq., F.G.S., F.Z.S.

The following conclusions were arrived at by the authors as the result of their observations:—

The gabbro or euphotide south of Mont-Genèvre is associated with serpentines, which were originally peridotites, and were not derived from the alteration of the gabbro. These coarsely crystalline rocks probably form a considerable subterranean mass, but have little importance at the surface.

They were broken through by dykes of dolerite and augite-andesite, and are now overlain by a great series of compact diabases and fragmental rocks, which has no direct connexion with the gabbro.

The Variolite of the Durance occurs *in situ* as a selvage on the surfaces of contact of these diabases among themselves, as blocks in certain fragmental rocks, which are regarded by the authors as tuffs, and occasionally as a selvage to the diabase dykes.

This product of rapid cooling was originally a spherulitic tachylite, and has become devitrified by slow secondary action. Variolite thus stands in the same relation to the basic lavas as pyromeride does to those of acid character.

The eruptive rocks in the Mont-Genèvre area are probably Post-Carboniferous, but their exact age cannot at present be determined.

There are several other areas of similar variolitic rocks among both the Alps and the Apennines of Piedmont and Liguria.

The best modern representatives of the conditions that produced

these rocks are to be found in the great volcanoes of Hawaii, and there is nothing either in their fundamental characters or in their mode of origin that cannot be paralleled among the products of causes now in action.

The authors expressed their indebtedness to Professors Bonney and Judd, as well as to those who have preceded them upon the classic ground of Mont-Genèvre.

2. "The Propylites of the Western Isles of Scotland, and their Relations to the Andesites and Diorites of the District." By Professor John W. Judd, F.R.S., F.G.S., &c.

The "Propylites" of von Richthofen and Zirkel constitute what has been aptly characterized by Rosenbusch as a "pathological variety" of the andesites. The relations of rocks of this type to the andesites and diorites in Eastern Europe and in the Western Territories of the United States have been made known to us by the researches of Dölter, Szabó, Becker, Hague and Iddings, and other petrographers.

The "felstones" described by the author of the present memoir as constituting the oldest series of the Tertiary volcanic rocks in the Western Isles of Scotland are now shown to belong to this interesting type. When found in an unaltered state, these rocks present remarkable analogies with the andesites of Iceland and the Faroe Islands, which have been so well described by Zirkel, Schirlitz, Osann, and Bréon. In the altered condition in which they usually occur, however, the Scottish rocks resemble in a not less striking manner the "propylites" of Eastern Europe and Western North-America.

The rocks in question vary in colour from white to dark grey, various shades of green usually prevailing among them. They have a specific gravity ranging from 2.4 to 2.9; the density diminishing as the silica percentage and the amount of glassy material in them increase; a lowering of the density of the rocks being also the result of extreme alteration. In their chemical composition these rocks were shown to agree with the pyroxene- and amphibole-andesites of other areas, and with propylitic forms of those rocks.

Very striking and remarkable is the amount of change that many of these Tertiary rocks have undergone—change that has equally affected their porphyritic constituents and the ground-mass in which these are imbedded. The feldspars are never fresh, but are more or less kaolinized, and not unfrequently converted into epidotes and other secondary minerals; the ferro-magnesian silicates are almost always changed into isotropic "viridite," or into various chlorites; while the titano-ferrite and magnetite have been converted either into "leucoxene" or into sulphides. The glass and microlites of the original ground-mass have in nearly all cases disappeared as the result of secondary devitrification.

The propylites are the oldest of the Tertiary lavas in the Western Isles of Scotland. They exhibit every gradation in minute struc-

ture, from holocrystalline forms (diorites) through various "granophyric" and "pilotaxitic" types into true vitreous rocks ("pitchstones"). They are found constituting lava-streams, which are usually short and bulky; eruptive bosses or "Quellkuppen;" and lenticular intrusions or "laccolites."

By carefully following in the field the much-altered rocks to points where they retain some of their original characters, the propylites can be shown to represent various interesting types of andesite and diorite. The amphibolic and micaceous rocks include hornblende-andesites, hornblende- and mica-andesites containing enstatite, diorites, and quartz-diorites. Among the pyroxenic rocks the most noticeable varieties are the labradorite-andesites, the pyroxene-andesites—of which both "trachytoid" and "vitrophyric" forms occur,—as well as examples of what have been called "diallage-andesites" (the nature of the pyroxene in which was fully discussed); these rocks are found passing into augite-diorites, and quartz-augite-diorites.

A microscopic study of these rocks enables us to investigate the processes by which they have acquired their peculiar characters. The chief and most widely operating cause of change is thus demonstrated to have been *solfataric action*; and this was shown to have accompanied the intrusion into the andesites of masses of igneous material of highly acid composition (granites and felsites). This solfataric action has been developed around each of the five volcanic centres described in 1874. A smaller and much more local cause of change—some of the results of which are strikingly contrasted with those of the wide-spread solfataric action—is found in the *contact-metamorphism* resulting from the intrusion into the andesites of masses of igneous rock of basic, intermediate, or acid composition.

The much-altered propylites of Tertiary age were shown to have their exact analogues among the older (Palaeozoic) lavas of Scotland and other districts. These rocks, which have been called "felstones," "porphyrites," &c., are andesitic lavas, some of which have suffered only from the action of surface-waters, while others among them must have been profoundly affected by solfataric action and converted into propylites, prior to the operation of the surface-agencies of change.

Forming a very striking contrast with the older Tertiary andesites (propylites), are the numerous scattered and generally small masses of rock which belong to a late period in the Tertiary, and constitute the youngest volcanic rocks of the British Islands. These rocks are found intersecting, in the form of dykes, the great sheets of olivine-basalt; or where poured out at the surface (as at the Sgùrr of Eigg and Beinn Hiant in Ardnamurchan), lie upon their greatly eroded surfaces. The rocks in question, which have the mineralogical constitution of augite-andesites, are remarkable for the wide variations in their aspect and chemical composition; and this was shown to result from *differences in the proportion of the crys-*

talline and glassy constituents to one another. Holocrystalline aggregates, of basic composition, are found passing, as the quantity of acid glass increases, into various "ophitic," "intersertal," and "pilotaxitic" types, finally assuming the "vitrophyric" form of "pitchstone-porphyrries"—rocks which have a distinctly acid composition. The rocks of the Tertiary dykes in Southern Scotland and the North of England, which have been described by Dr. A. Geikie, Mr. Teall, and other authors, were shown to agree with these later Tertiary andesites, both in their mineralogical constitution and in the peculiar phases which they present to us. The latest Tertiary ejections were shown in 1874 to bear the same relations to the five grand volcanoes of the Western Isles which the chains of "pays" in Auvergne do to the great central volcanoes of that district; and this conclusion is strikingly confirmed by petrographical studies of which the results were given in the present memoir.

XXXI. *Intelligence and Miscellaneous Articles.*

NOTE ON THE GRADUAL ALTERATION IN GLASS PRODUCED BY ALTERING ITS TEMPERATURE A FEW DEGREES. BY SPENCER U. PICKERING, M.A.*

THE alteration experienced by glass when heated to temperatures above 50° C. is well known, but I do not think that it has previously been noticed that a rise or fall of even a few degrees at ordinary temperatures will produce an appreciable alteration of a similar nature.

That such is the case, however, the following experiments will show. During the course of a series of density-determinations, in which the apparatus used consisted of an ordinary 25 cub. cent. density-bottle with perforated stopper—but of which the stopper was so accurately ground that it made the instrument thoroughly reliable—the water-contents of the bottle were frequently determined. Between November 1887 and May 1888, during which time the temperature of the laboratory had been kept at about 18°, no appreciable alteration in the capacity occurred, the values all being within .0002 grm. of 25.0070 grm., and this in spite of the fact that the bottle had been temporarily heated to temperatures as high as 35°. But during November and December of the latter year the temperature of the laboratory had been maintained 10° lower than during the previous twelve months, and the effect of this lowering on the bottle was such that its water-contents, measured at the same temperature, were .001 gram less. Although the amount of this contraction is small, the following values will, I

* Communicated by the Author.

think, place its existence beyond doubt: they were determined, as will be seen, at various temperatures between 6° and 28°.

The gradual contraction does not appear to have ceased at the end of the seventeen days' exposure of the bottle to 8°, nor does it seem to have been affected by the temporary heating of the bottle to the higher temperatures at which its contents were determined.

In the last column is given the weight of the bottle itself on the various dates: it shows a slight gradual decrease owing to wear; but this wear, even if it took place entirely on the inside, would not be sufficient to account for a tenth part of the decrease in the weight of the contents.

Alteration in the Capacity of Glass Bottle while being kept at 8°, after it had been previously kept at 18°. Contents measured at t° .

$t=$	6°.	8°.	10°.	12°.	Bottle alone.
Nov. 8	25·0301	15·7192
Dec. 3	25·0317	25·0288	25·0245	15·7188
" 12	25·0293	15·7188
" 16	25·0311	25·0289	25·0264	25·0228	15·7187
" 17	25·0269	15·7186
$t=$	14°.	14°.*	16°.*	28°.	
Nov. 30	24·9535	15·7191
Dec. 3	25·0916	24·9532	15·7188
" 7	44·4345	43·6239	24·9519	15·7187
" 17	25·0182	44·4309	43·6207	15·7186

* The bottle contained sulphuric-acid solutions instead of water in these cases.

Just as cooling the bottle for a few degrees induces a gradual contraction, so does heating it induce a gradual expansion. After the contents measured at 28° had been reduced on December 7 to 24·9519 grams, they were found to have increased to 24·9532 grams by April in the following year, the bottle in the mean time having been kept at the higher temperature of 12°–15°. Again: on December 3, 1889, after the bottle had been exposed for some time to a temperature of about 10°, its contents at 18° were found to be 25·0066 grams; it was then heated at 30°–35° for three days, after which they had increased to 25·0073 grams.

The maximum alteration in capacity noticed in any of the above experiments is ·0001 of the total volume, and an alteration of this

magnitude occurring in the bulb of a thermometer would mean a displacement of the zero-point by $\frac{1}{15}^{\circ}$.

ON A TELETHERMOMETER. BY PROF. DR. J. PULUJ.

The author gave the following abstract of a long paper on this subject :—

The present paper contains the description and theory of an apparatus, which renders it possible to transfer to a distance the indications of any given temperatures. The construction of the telethermometer depends on the use of two conductors, the resistance of which varies with the temperature in opposite directions, and which form the thermometric part of the apparatus. The latter consists of a small glass tube closed at both ends, which contains a carbonized strip and a spiral of platinum wire, and which is filled with hydrogen in order to conduct the better. The carbon strip and the iron spiral form two branches of a Wheatstone's bridge, and by means of three wires are connected with a measuring-scale which has an empirical scale of temperature in Centigrade degrees. The resistance of the carbon strip decreases with the temperature, while that of the iron increases, and in accordance with this the zero of the difference of potential is altered. The temperature may be determined either by means of an astatic galvanometer, or by a telephone with a microphonic contact-breaker in such a manner that contact with the measuring-wire is deferred until the galvanometer shows no deflexion, or the telephone gives no sound. The telethermometer renders it possible to determine temperatures at a distance of 1 km. to within $0^{\circ}\cdot 1$ C.

In the theoretical part of the paper the displacement of the contact along the wire is calculated, and the graduation of the telethermometer is completely discussed; this is followed by a calculation of the correction of the scale for temperature, and the proof is given that a rise of temperature of the wire bridge has no influence on the indications of the telethermometer. It is shown in conclusion how the telethermometer may be used as an indicator of temperature, which automatically gives the temperature at any instant.—*Wiener Berichte*, Oct. 10, 1889.

ON THE MEASUREMENT OF ELECTROMOTIVE CONTACT FORCES OF METALS IN DIFFERENT GASES, BY MEANS OF THE ULTRA-VIOLET RAYS. BY A. RIGHI.

Since, as is shown by the earlier experiments of the author, ultra-violet rays bring to the same potential bodies which are very close to one another, the differences of potential of contact can by this

means be very conveniently measured. It is only necessary to measure the deflexion in the electrometer connected with the plate after it has been put to earth for an instant while ultra-violet rays have been allowed to fall on the plate through the net. The light of a zinc-carbon arc-lamp was always used. The plates of ordinary metal and carbon were in air, or in a bell-jar filled with gases or moist air. The net was of zinc, brass, or platinum. From the differences of the observations with the same net and different plates the differences of potential between the latter can be deduced. In dry and moist air and in carbonic acid they are the same; in hydrogen they are so for C, Bi, Sn, Cu, Zn, but different for Pt, Pd, Ni, Fe. When hydrogen is gradually allowed to enter, these metals behave as if they were gradually oxidizable in air. For platinum against a zinc net the difference of potential reduces from 1.12 in air to 0.69 in hydrogen. On the fresh addition of air the electromotive force returns in the opposite direction to its original value. Metals such even as tin and bismuth behave in ammoniacal air as if they were less oxidizable, and therefore the opposite of what obtains with hydrogen. Here also in air the initial electromotive force is restored. In coal-gas, carbon, copper, and platinum behave like oxidizable metals. With a platinum net and a copper plate the sign of the electromotive contact-force is changed when coal-gas is admitted instead of air.—*Rendic. Lincei* [5] p. 860, 1889; *Beiblätter der Physik*, xiv. p. 69.

MR. ENRIGHT'S EXPERIMENTS.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

When Mr. Enright described his attempts to prove that contact could electrify hydrogen, in 'Nature,' August 18, 1887, I wrote to that Journal (vol. xxxvi. p. 412) to point out that all he had observed could be expressed in a few lines as due to the well-known frictional electrification of spray. The length of his communication to the Physical Society, printed in your January number, may perhaps have deterred a critic from reading it. But he makes no serious attempt to meet my obvious objection, and so far as experiments so crude can negative anything they negative his own contention.

Yours faithfully,

OLIVER J. LODGE.

Liverpool, February 15, 1890.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1890.

XXXII. *On Magnetization in Strong Fields at Different Temperatures.* By H. E. J. G. DU BOIS, of the Hague*.

[Plate VIII.]

§ 1. **INTRODUCTORY.**—Prof. Rowland, in summarizing his well-known magnetic researches (1873), thus carefully expresses himself:—

“(7) Iron, nickel, and cobalt all probably have a maximum of magnetization, though its existence can never be entirely established by experiment, and must always be a matter of inference; but if one exists, the values must be nearly as follows at ordinary temperatures. Iron when $\mathfrak{B}=17500$ or when $\mathfrak{I}=1390$; nickel when $\mathfrak{B}=6340$ or when $\mathfrak{I}=494$; cobalt when $\mathfrak{B}=10000$ (?) or when $\mathfrak{I}=800$ (?)”†. Until lately, nothing decisive was done in the matter, apart from occasional announcements of \mathfrak{I} having been found > 1390 for iron; and Rowland’s values had to be adopted by experimenters, including myself (Phil. Mag. Nov. 1887)‡. Mr. Shelford Bidwell’s experiments on the lifting-power of divided ring-electromagnets (up to $\mathfrak{H}=585$) furnish important

* Paper read before the Physical Society of Glasgow University, Nov. 8, 1889; a synopsis of results had been communicated to the Brit. Assoc., Newcastle (see Proceed. Sect. A, Sept. 17, 1889 Report).

† Rowland, Phil. Mag. [4] xlviii. p. 339 (1874); reduced to C.G.S. units.

‡ Compare Fromme’s comments, Wied. Ann. xxxiii. p. 234 (1888).
Phil. Mag. S. 5. Vol. 29. No. 179. April 1890. 2 A

evidence for the continual increase of the Induction, proportional to the square root of the weight supported. However, I cannot quite agree with the author's way of calculating the curve of magnetization*. Quite recently Messrs. Ewing and Low † published the final results obtained with their ingenious "isthmus" method, which disprove the existence of a limit to \mathfrak{B} , the induction having been forced up to over 45,000 C.G.S. The authors further conclude that the magnetization remains sensibly constant throughout the extensive range of magnetizing field (2000 to 20,000 C.G.S.) which they were the first to apply.

§ 2. Mainly with a view to check these results by an altogether different method, and to obtain more accurate data than the isthmus method, as developed at present, appears capable of supplying, I undertook the experiments to be described. Excepting Mr. Bidwell's 585 C.G.S., fields over a few hundred units hardly appear to have been applied in coils; I therefore began with a powerful coil giving up to 1300 C.G.S. Thence upward to 13,000 an optical method, based on Kerr's phenomenon ‡, was used. I have also studied the effect of temperature with these strong fields; considerable interest having been lately attached by various authors to theoretical thermomagnetic speculations; and thermomagnetic motors having been proposed by Thomson-Houston, Schwegdoff, Stefan, Edison, and others §. In conclusion, the important part played by magnetization in affecting the properties of matter is discussed.

Throughout this paper I shall as usual denote by: \mathfrak{H} , magnetic intensity; \mathfrak{B} , induction; when the values of these quantities inside the metal are considered, they are denoted by \mathfrak{H}' and \mathfrak{B}' ; \mathfrak{I} , magnetization; D , density; $\mathfrak{S} = \mathfrak{I}/D$, specific

* The magnetic intensity \mathfrak{H} in the thin air-films between the halves of the ring evidently equals \mathfrak{B}' , the induction in the iron. Now the tractive force per unit section is equal to the tension in the lines of force

$$G = \mathfrak{H}^2/8\pi = \mathfrak{B}'^2/8\pi = 2\pi\mathfrak{I}^2 + 3\mathfrak{H}' + \mathfrak{H}'^2/8\pi; [\therefore \mathfrak{B}' = \mathfrak{H}' + 4\pi\mathfrak{I}]$$

(for notation, see § 2). This adaptation of Maxwell's formula by Rowland, Mr. Bidwell (Proc. Roy. Soc. xl. p. 492, 1886) finds "clearly erroneous," though I fail to see why. He adopts the formula

$$G = 2\pi\mathfrak{I}^2 + 3\mathfrak{H}';$$

the missing term $\mathfrak{H}'^2/8\pi$ appears, from the action-at-a-distance point of view, to correspond to the mutual electrodynamic attraction of the two half-coils, neglected by Mr. Bidwell.

† Ewing and Low, Phil. Trans. clxxx. p. 221 (1889).

‡ See du Bois, Wied. Ann. xxxix. p. 25 (1890); transl., Phil. Mag. ante, p. 253; the paragraphs of which will be referred to as *loc. cit.*

§ See Stefan, Wien. Berichte, xcvii. 2, p. 70 (1888). Kittler, Handbuch der Elektrotechnik, ii. p. 47 (1890).

magnetization, *i. e.* moment per unit mass ; θ , temperature ; ϵ_0 , rotation of plane of polarization ; K , "Kerr's constant." C.G.S. units are tacitly assumed, wherever the contrary is not expressly stated ; compare *loc. cit.* § 5.

I. MAGNETOMETRIC OBSERVATIONS.

§ 3. *Apparatus.*—Four elongated ovoids (prolate ellipsoids of revolution) of length 18 centim. and diameter .6 centim. (ratio 1·30) were prepared and could be uniformly magnetized in the coil. On account of their non-endlessness a correction of .052 \mathfrak{J}^* had to be subtracted from the field \mathfrak{H} of the coil in order to obtain the real magnetic intensity \mathfrak{H}' inside the ovoid. The following metals were tested :—

(a) Soft Swedish iron, carefully annealed : $D=7\cdot82$.

(b) Hard English cast steel, yellow-tempered at 230° : $D=7\cdot78$.

(c) Hard-drawn best nickel wire : $D=8\cdot82$ (from the "Nickelwalzwerk" in Schwerte, Westphalia) ; stated by the makers to contain 99 per cent. Ni, besides SiO_2 and traces of Fe and Cu.

(d) Cast cobalt : D about 8·0 (from Messrs. Johnson and Matthey). My friend Dr. Serda kindly analysed this for me with the following result :—Co 93·1 per cent., Ni 5·8 per cent., Fe .8 per cent., Cu .2 per cent., Si .1 per cent., C .3 per cent. Rather unsatisfactory brittle material ; the ovoid broke in the lathe ; it was thought best to scrape the fractured ends truly plane, and to hold them tightly pressed together in a brass tubular screw-and-nut arrangement †.

The coil was wound to the following dimensions : length 30 centim. ; inner diameter 4 centim. ; outer diameter 12 centim. ; 12 layers, each of 90 turns, of double cotton-covered shellacked wire, .25 centim. in diameter ; resistance cold .9 ohm. It could be surrounded by an ice-jacket ; with a dynamo-current of 32 amp. almost a kilo-watt of activity was being dissipated in it, sufficient to melt a kg. of ice every five minutes. In other cases the coil was electrically heated.

§ 4. The ovoids, fixed inside the coil, could be maintained at 0° or 100° by ice or steam properly applied. The arrangement for heating them over 100° and the mode of determining the field are described, *loc. cit.* §§ 4 and 14. The whole of this apparatus was placed in Gauss's "first position," about 135 centim. due east of a magnetometer. It was

* See Maxwell, Treatise, 2nd ed. ii. § 438, form. (14).

† See J. J. Thomson and Newall, Proc. Cambr. Phil. Soc. vi. p. 84 (1887) ; Ewing and Low, Phil. Mag. [5] xxvi. p. 275 (1888).

attempted to compensate the very considerable action of the coil alone by that of another similar one, placed due west and in the same circuit. Great difficulty was experienced with this, principally due to heating of the coils and parasitic action of distant current leads. Finally the idea of total compensation had to be given up, and the remaining difference was each time carefully determined and corrected for. The earth's horizontal intensity at the magnetometer's site was measured once for all; its fluctuations being followed with one of Prof. F. Kohlrausch's local variometers. Thus the magnetic moments of the ovoids could be accurately obtained in absolute measure.

§ 5. *Preliminary trials.*—I began by trying whether there was a perceptible influence of magnetic history in general; or of the hysteresis, due to its latest phases, in particular. The ovoids were therefore made to pass through various magnetic ordeals, as descending or ascending currents, reversals, &c. None were found, however, to have an appreciable effect, except with fields below 150 C.G.S., say, where such an influence occurred, though slightly. The reasons for this are no doubt:—(1) the ovoids had too little of endlessness to exhibit much hysteresis in any case; (2) the slightly pulsating machine-current effectually counteracts it by its shaking action; and (3) probably hysteresis really comes less to the foreground with such strong magnetizing fields.

However this may be, I was thereby free to magnetize in whatever manner I chose; as a rule, two magnetometer-readings were taken with currents reversed. The moment for a given temperature may thence be plotted in a loopless curve as a function of \mathcal{H} only, provided the latter exceed 100 C.G.S. say. Neither was I sensibly troubled with the well-known acyclic shaking-in action of temperature-variations; perfectly consistent results being obtained with strong fields whether on heating or on cooling. Accordingly the moment due to a given magnetic intensity may be considered a function of the temperature only.

§ 6. *Magnetic curves.*—After much hesitation I decided not to plot \mathcal{M} as usual, but the specific magnetization \mathcal{S} . The principal reason for this was that the results became more comparable by thus eliminating the density, which depends on temperature and other physical conditions of the material, and could moreover not be determined for the electrolytic metals tested (§ 8). In fact, magnetism being an essentially molecular phenomenon, it is for certain purposes more rationally

referred to unit mass, which always contains the same number of molecules, than to unit volume, which does not. In Pl. VIII. fig. 1 the long curves represent $\mathfrak{S} = \text{funct. } (\mathfrak{H}')$ over a range evident from the scale of abscissæ. The origins do not occur in the diagrams, excepting that for nickel, which is joined to the first experimental point \odot in a manner approximately estimated from known data. From these curves others may readily be calculated; in particular, those representing $\mathfrak{I} = \text{funct. } (\mathfrak{H}')$, which will be referred to below.

§ 7. *Effect of temperature.*—The upper curves of magnetization for iron and steel correspond to 0° . It will be seen that at first they almost coincide with those for 100° , but that the difference increases towards larger abscissæ. For \mathfrak{H}' constant*, equal to about 900 C.G.S., $\mathfrak{S} = \text{funct. } (\theta)$ was then determined. It is represented by the short temperature-curves to the left of fig. 1, plotted to the separate scale of abscissæ. They all show a decrease of \mathfrak{S} ; the latter evidently always being above its critical value, below which it is known to increase on heating. The nickel curve falls off less abruptly than it is known to do for weaker magnetizing fields. Hence in an infinitely strong field the magnetization of all these metals would probably begin by decreasing at a quicker rate still; then to fall off without any abruptness towards practically vanishing values (see § 13).

On the hypothesis of magnetic molecules, this case corresponds to the temperature-variation of the *individual molecular moments*, because the supposed infinite field would direct the axes of all the molecules parallel to itself. It is the simplest case; the abrupt changes and other complications observed with ordinary fields being due to the action of temperature on the *direction of the molecular axes*. All this was theoretically pointed out by Prof. G. Wiedemann†. As far as I can see, my results nowhere contradict any previous thermomagnetic researches, conducted with much lower fields, though partly at higher temperatures, by G. Wiedemann, Rowland, Baur, Wassmuth, Ewing, Berson, Ledebøer, Tomlinson, J. Hopkinson, and others.

§ 8. *Additional experiments* were made on material slightly differing in condition or quality from that above defined (in § 3). Annealing the hard-drawn nickel caused the

* Of course it was the current, and with it the field \mathfrak{H} , which was actually kept constant; but the increase of $\mathfrak{H}' = \mathfrak{H} - 0.52\mathfrak{I}$, amounts to but 2 per cent. even when, as with nickel, \mathfrak{I} falls off from 500 to 0.

† *Lehre v. d. Elektrizität*, iii. § 892.

magnetic curve to rise much more rapidly at first without, however, attaining in the end to values beyond those of the unannealed metal. The yellow-tempered hard steel was further tempered dark blue and finally annealed at red heat without any very marked change in the general character of the curve ensuing.

The values of \mathfrak{S} , found for iron and nickel, are 216.1 and 54.0 respectively at 25° , as interpolated on the temperature-curves of fig 1. Thin sheets of electrolytic iron and nickel were now prepared in the shape of oblong ellipses and weighed. They were subjected (at ordinary temperature) to a field of 900 C.G.S., and their moments approximately measured with the following results:—

a. Iron, about .05 centim. thick, originally intended for printing Russian banknotes, and kindly given to me by Prof. F. Kohlrausch : $\mathfrak{S}=211.4$, 30 per cent. of which was residual.

b. Iron, about .005 centim. thick, which I electrolytically obtained from the so-called Varrentrapp bath : $\mathfrak{S}=213.7$, 50 per cent. of which was residual.

c. Nickel, about .015 centim. thick, from citrate of nickel : $\mathfrak{S}=53.5$, 20 per cent. of which was residual.

Electrolytic cobalt could not be got in films sufficiently thick for this purpose. The results appear to warrant the conclusion that with these very strong magnetizing fields much does not depend on the quality of the metal, as long as it is tolerably pure. Nor has its condition, as resulting from the mechanical and thermal treatment previously applied, any sensible influence. Of course the experiments in this paragraph are meant to be novel only with respect to the strong fields applied.

II. MAGNETO-OPTIC OBSERVATIONS.

§ 9. *Method and Apparatus.*—As the isthmus method is based on the principle of tangential continuity of \mathfrak{H} and discontinuity of \mathfrak{B} ($\mathfrak{H}'=\mathfrak{H}$ and $\mathfrak{B}'>\mathfrak{B}$), so the method to be described may be said to rest on the normal discontinuity of \mathfrak{H} and continuity of \mathfrak{B} ($\mathfrak{H}'<\mathfrak{H}$ and $\mathfrak{B}'=\mathfrak{B}$). In addition, the normal component of \mathfrak{B} is measured by the rotation impressed upon plane-polarized light normally reflected from the magnetized metal. In order to obtain the former the latter has only to be divided by a factor, which I have proposed to call “Kerr’s constant” (*loc. cit.* § 24).

The optical apparatus used for accurately measuring the rotation of red light has been described at length (*loc. cit.*

§§ 2, 16). Small disks M were turned out of the same material as that above defined (§ 3), and polished on one side. These mirrors were fixed to one pole P_1 of a Ruhmkorff electromagnet (see Pl. VIII. fig. 3, full size). On its way towards the reflecting surface and back the light passed through the narrow bore of the other pole P_2 , which thus screened off all but a small central patch of the mirror. Here the lines of induction evidently issue normally from the metal for reasons of symmetry. P_1 and M could be kept very nearly at 100° by means of a steam-jacket JJ .

§ 10. A very thin standard glass-plate G , silvered (S) at the back, could be placed immediately in front of the mirror. The light then being reflected in it suffers a double magnetic rotation in the glass; this affords a measure for the field \mathfrak{H} directly in front of the metal, equal, by the principle of continuity alluded to, to the induction \mathfrak{B}' immediately inside it. The glass plate had previously been magneto-optically standardized by comparison with bisulphide of carbon, whose Verdet's constant is known from the determinations of Lord Rayleigh and Koepsel; such standards are very convenient. Owing to Ruhmkorff's well-known construction the ray has to pass through one of the coils on its way to and from M through P_2 . The ensuing very slight double rotation in the magnetized air must be proportional to the current, and may be calculated from the data of H. Becquerel, Kundt and Röntgen. It was in every case corrected for, the maximum value being $+ \cdot 3'$; I have actually observed about this rotation with a silver mirror.

§ 11. *Results.*—The first thing experimentally obtained was the curve $\epsilon_0 = \text{funct. } (\mathfrak{B}')$, whose ordinates must be and were actually found proportional to those of $\mathfrak{I} = \text{funct. } (\mathfrak{B}')$; the latter being calculated from $\mathfrak{S} = \text{funct. } (\mathfrak{H})$, as far as this goes (see § 6). In order further to exemplify the somewhat complicated mode of calculation the numbers for cobalt and nickel are given in Table I. Here the italics are the three highest corresponding values of \mathfrak{I} and \mathfrak{B}' , indirectly given by the magnetometric method; the ordinary type refers to the five highest corresponding values of ϵ_0 and \mathfrak{B}' , obtained magneto-optically with all possible accuracy †. The value of \mathfrak{I} marked * is interpolated from those above and below; it corresponds to the rotation ϵ_0 printed to its left; the ratio of

+ *I. e.* from 30 observations of the analyser's azimuth; the smaller values of ϵ_0 were based on 4 observations and measured only in order to approximately check the whole method by the proportionality of ordinates above alluded to.

TABLE I.

Cobalt.				Nickel.			
θ .	\mathfrak{B}' .	ϵ_0 .	\mathfrak{S} .	θ .	\mathfrak{B}' .	ϵ_0 .	\mathfrak{S} .
100°	14120	1058	100°	5980	437
100	14180	-20'97	1060*	100	6420	-7'25	453*
100	14410	1070	100	6490	456
100	14650	1081	100	6810	461
100	16750	-22'45	1134†	100	9920	-8'29	518†
100	19550	-23'24	1174†	100	12850	-8'36	522†
100	21710	-23'38	1181†	100	16250	-8'43	527†
100	23330	-23'60	1192†	100	19290	-8'40	525†
0°	23330	-24'39	1232×	0°	19290	-9'27	579×

both quantities gives Kerr's constant for red light, in minutes per unit magnetization, as follows:—

	Cobalt.	Nickel.	Steel.	Iron.
ϵ_0 . .	-20'97	-7'25	-24'81	-22'99
\mathfrak{S} . .	1060	453	1531	1669
K. . .	-0198	-0160	-0162	-0138

Inversely the four remaining values of ϵ_0 were now divided by K, thus giving $\mathfrak{S} = \text{funct. } (\mathfrak{B}')$ marked † in the Table. From this again $\mathfrak{S} = \text{funct. } (\mathfrak{H})$ could be calculated, which thus forms a continuation of the curves obtained before (in § 6).

§ 12. In fig. 2 the results of both methods are combined into continuous magnetic curves, now extending, at least in the case of nickel, from $\mathfrak{H}' = 150$ to $\mathfrak{H}' = 13,000$ C.G.S. The scale of abscissæ is ten times smaller than in fig. 1, and the additional points ⊙ are those derived from the optical method. As the strongest field \mathfrak{H} of the Ruhmkorff attained about 25,000 C.G.S. it is evident that the maximum intensity \mathfrak{H}' , obtainable inside the metal ($\mathfrak{H}' = \mathfrak{H} - 4\pi\mathfrak{S}$), is less the more strongly magnetic the metal used. Thus in fig. 2 the abscissæ extend to 8500 for cobalt, to 4500 for steel, to but 2500 for iron; the latter's curve is therefore not continued beyond $\mathfrak{H} = 1200$, the point reached in fig. 1; the more so as the iron gave somewhat irregular results on account of the mirror's polish not being perfect. The rotational dispersion being much greater for iron and steel contributed to make the

optical measurements with the only approximately homogeneous "red" light less accurate than for cobalt and nickel (*loc. cit.* § 21); another reason for attaching most importance to these latter's curves.

§ 13. Nearly all optical observations were made, with steam on, at 100° ; cooling to 0° would not do on account of the dew condensing on the mirror. A few measurements were, however, made with the strongest fields at ordinary temperature; the rotations proved greater than at 100° in every case, and their values for 0° were obtained by simple extrapolation; they are given at the bottom of Table I. The values of \mathfrak{Z} marked \times were calculated on the assumption of absolute invariability of Kerr's constant with temperature, whereas I have only shown the variations to be less than the limit of experimental errors (a few per cent. per 100° , *loc. cit.* § 15). The corresponding values of \mathfrak{S} are marked $\times 0^{\circ}$ in the diagrams of fig. 2 for steel, cobalt, and nickel. From a comparison with the short temperature-curves of fig. 1 it would appear (always on the above assumption) as if the decrease of magnetization from 0° to 100° were much more marked for fields of thousands of units than for lower ones. The conclusion of § 7 is based on this inference.

§ 14. *Magnetite* (see *loc. cit.* § 17).—Curve I. of fig. 4 represents $\epsilon_0 = \text{funct. } (\mathfrak{B}')$, experimentally determined for a small crystal of magnetite by purely optical observations (at ordinary temperature); its ordinates must be proportional to those of $\mathfrak{Z} = \text{funct. } (\mathfrak{B}')$. Now the latter function is unknown for this material, but it may be asserted to start from the origin very nearly as a straight line $\mathfrak{Z} = \mathfrak{B}'/4\pi^*$. On inspection of curve I. the two observed points \odot nearest the origin are accordingly seen to lie almost in line with it. Now multiplication of these two values of ϵ_0 into the corresponding ones of $4\pi/\mathfrak{B}'$ is easily seen to give Kerr's constant as $+0.0122$ and $+0.0115$ for the two points respectively; the mean value $+0.012$ will be sufficiently near the truth for our present purpose.

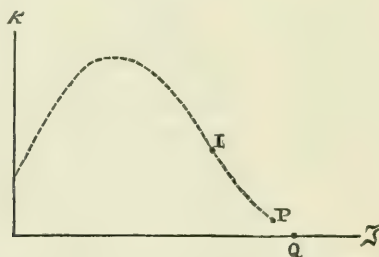
We consequently divide the ordinates of $\epsilon_0 = \text{funct. } (\mathfrak{B}')$ by $.012$ and thus obtain $\mathfrak{Z} = \text{funct. } (\mathfrak{B}')$ in absolute measure. Thence $\mathfrak{Z} = \text{funct. } (\mathfrak{B}')$ is easily calculated and plotted as curve II. (fig. 4). The magnetization evidently tends towards a limit not much above 350 C.G.S., somewhat less than that for nickel. Our magneto-optic method has thus given an absolute magnetic curve, at least approximately,

* du Bois, Wied. *Ann.* xxxi. p. 952 (1887); *Phil. Mag.* Nov. 1887.

without any magnetic observations having been made. In fact these are quite out of question in the present case; and accordingly no absolute data have ever been given for magnetite or loadstone that I am aware of.

III. CONCLUSION.

§ 15. There can be no doubt that the curves of fig. 2, especially those for cobalt and nickel, show a tendency to a limiting value of magnetization. This of course can never actually be observed, but the values of \mathfrak{I} can hardly exceed 1630, 1200, 530 C.G.S. respectively for the steel, cobalt, and nickel used (at 100°). Though, as explained in § 12, iron unfortunately happened to give the least trustworthy results, I may infer from my observations that the value 1750 cannot be far from the truth (also at 100°). As regards the important question whether the approach is an asymptotic one, or whether \mathfrak{I} reaches a maximum with finite values of \mathfrak{H} , thence to rediminish*, I cannot pretend to decide it any more than Messrs. Ewing and Low. The apparent slight decrease in the case of nickel (see Table I., $\mathfrak{I}=525$) is within the range of experimental error.



Accordingly the general type of the well-known susceptibility curves $\kappa = \text{funct.} (\mathfrak{I})$ has the point of inflexion I, as was indeed first shown for iron by Fromme and Haubner (see § 1, footnote). Its continuation beyond the final experimental point P is a matter of inference. If there be an asymptotic limit to \mathfrak{I} , the curve will cut the axis of abscissæ in a point Q, and the shape of the end PQ will depend on the law of approach of \mathfrak{I} ; *e.g.* if the approach be like that

* See Maxwell, Treatise, ii. § 844. It may be well to observe that even in a field of 35,000 C.G.S. the magnetization of bismuth, the most diamagnetic metal known, would reach but $-.5$, *i.e.* $-\frac{1}{20}$ per cent. of the limiting value for nickel, so that its superposition on the latter would probably escape observation.

of a hyperbola towards its asymptote PQ will be very nearly IP tangentially produced. These curves of course have nothing to do with those representing the permeability, $\mu = \text{funct. } (\mathfrak{B})$, which have been shown by Messrs. Ewing and Low to tend towards the asymptote $\mu = 1$, for $\mathfrak{B}' = \infty$.

§ 16. The general conclusions of these physicists are entirely corroborated by the present experiments, conducted on altogether different lines. I believe all doubts, that have occasionally arisen as to the existence of a limit of Magnetization, will thereby be dissipated. In fact this quantity appears about to regain its physical importance, which has lately been perhaps too much transferred to Induction. This I will now endeavour to show, without thereby in the least wishing to contest the great advantages of induction in the mathematical theory, as well as in the practical applications of electromagnetism.

In 1842 the late James Prescott Joule* enunciated the law that the elongation of unstrained iron is proportional to the square of the magnetization applied. The same has recently been shown by M. Goldhammer to hold for the decrease of electric conductivity†; and it can hardly be doubted that thermal conductivity varies in the same manner.

I have shown the optical rotation to be entirely dependent on and directly proportional to the magnetization on reflexion as well as on transmission (*loc. cit.* § 23, and *Phil. Mag.* Nov. 1887). Hall's effect probably follows the latter law‡, and it is natural to suppose that the three analogous phenomena discovered by Messrs. v. Ettingshausen and Nernst will prove no exceptions.

§ 17. I therefore entirely agree with M. Goldhammer, where he points out the probability of this general law:—

“Magnetization affects all physical properties of metals in a way generally depending on its direction. Whenever the ensuing changes are odd functions of the magnetization (both simultaneously reversing their sign), they are simply proportional to it. In the case of even functions (always having the same sign), they are proportional to its square.”

This statement is an expansion of ideas put forth by Sir

* Joule, Reprint of Papers, i. p. 245.

† Goldhammer, *Wied. Ann.* xxxvi. p. 823 (1889); *Procès-verbaux, Paris Electr. Congress*, Aug. 30, 1889.

‡ This statement, well worth safely establishing by experiment, is based on the following evidence:—1. By Hall, curve for Ni, *Phil. Mag.* [5] xii. p. 166 (1881); 2. Residual effect in steel, *Phil. Mag.* [5] xix. p. 419 (1885); 3. Behaviour of conducting strips of various thicknesses, *Sillim. Journ.* [3] xxxvi. p. 131 (1888); 4. By v. Ettingshausen and Nernst, table for Co and Ni, *Wien. Ber.* xciv. 2. pp. 585, 587 (1886).

W. Thomson in 1855*. The relation assumed to exist between the optical phenomena and Hall's effect (as extended to displacement currents) by Messrs. Rowland, H. A. Lorentz, and van Loghem† appears in a certain sense as one of its particular cases. In conclusion, it may be remarked that the above phenomena are not actions at a distance, but actually occur on the selfsame spot as the magnetization, which thus appears to be their common cause, and to have a real physical existence.

APPENDIX.

On Manganese Steel.

The optical method having proved a valuable aid in the case of magnetite, it occurred to me to apply it for scrutinizing the behaviour of manganese steel. A piece of bar and some wire was kindly supplied to me by Mr. Hadfield, of the Hecla Works, Sheffield. Chemical analysis, for which I am again indebted to Dr. Serda, gave 87.1 per cent. Fe, 11.8 per cent. Mn, .3 per cent. Si, and some C. It is susceptible of an excellent polish, rather better than that on ordinary steel. However, I find it somewhat more liable to rust; after some months the polished surface showed small specks of oxide under the microscope. Rough magnetometric measurement, with the strong fields of the coil, gave an apparently constant susceptibility of only .001, or permeability 1.013 ‡; about 25 per cent. of the magnetization being residual.

On magneto-optic examination, in the manner above developed, negative rotation was found in every case. But its numerical value varied considerably according as different patches of the same polished surface were made to reflect, or as different mirrors, ground on to the same piece, were tried. The rotation on a given patch was not proportional to the

* Sir W. Thomson, Reprint of Papers, ii. p. 178.

† See Wied. *Beiblätter*, viii. p. 869 (1884).

‡ Literature on p. 34 of Mr. Hadfield's paper read before the Iron and Steel Institute, Edinburgh, 1888; further, Barrett, Proc. Roy. Soc. Dubl. vi. p. 107 (1888). Results of experiments made at the German marine observatory of Wilhelmshaven are given in *Ann. d. Hydrogr.* xvii. p. 177 (1889), though not in absolute measure; however, on considering the data given, the susceptibility may be estimated at .005 for the thin bar, and .0015 for the thick bar used. Ewing and Low, *loc. cit.*, find the permeability much larger, viz. 1.4, and constant for magnetizing fields between 2000 and 10,000 C.G.S. This seems to show that the magnetic properties of manganese steel are exceedingly variable from one sample to another. [The same conclusion is arrived at by Dr. Paul Meyer, in an article published quite recently (*Elektrotechnische Zeitschrift*, x. p. 582 (1889) after the reading of the present paper.]

field of the Ruhmkorff, as the constant permeability at first led me to expect, but tended towards a limit. The largest rotation obtained was about $\frac{1}{3}$ of the maximum for iron. All this appears to me to show the material to be essentially heterogeneous, relatively strongly magnetic layers being interposed between the feebly magnetic mass. Probably the structure on the whole is laminar, and so fine-grained that to ordinary chemical mass-tests it appears perfectly homogeneous. The ultimate heterogeneousness is only revealed by the magneto-optical method, in which the action is restricted to a surface patch a few millim. in diameter and a fraction of a wave-length in thickness. Microscopical examination of a mirror showed a faint indication of streaks in the polished surface, and the specks of rust alluded to appeared to be arranged in definite configurations. The crystallographic method of corrosive etching was now resorted to: a drop of dilute nitric acid produced a peculiar network of microscopical surface figures, not revealed by a common steel mirror after the same treatment. This affords another proof for the heterogeneousness of manganese steel, which thus appears to be rather an unsatisfactory alloy for the physicist to deal with*, however interesting it may be to the engineer.

I believe great care should be taken in drawing conclusions from the greater or less attraction of manganese steel filings by strong magnets, this attraction proving an altogether false criterion. I have not been able to file my samples; but small particles scratched off with a glass-cutting diamond were readily attracted by any magnet. A piece of wire was then drawn out to $\frac{1}{3}$ millim. diameter, and a number of small bits, about 1 millim. long, cut off. These also behaved like a heap of filings, and were attracted by a magnet as long as separate. But on kneading them together with very little wax, the lump was as unaffected by the magnet as a larger piece of wire or bar.

I think all this is only due to the diminutive dimensions of the particles, and to nothing else, because they may thus come very near the edges of the steel magnet. Here the space-variation of H^2 , on which the attraction depends, probably is considerable. In connexion with this it may be remembered that mineralogists extract ferruginous minerals,

* In fact the ordinary theory of magnetic induction ceases to be applicable to heterogeneous solids; all results obtained by the magnetometer, isthmus, Quincke's, or any other method must therefore be regarded as untrustworthy. If, for example, the laminae are, on the whole, perpendicular to the field, the constant permeability, found by Messrs. Ewing and Low, comes out quite naturally.

though quite unmagnetic in large lumps, out of the crushed rocks with magnets. Magnetic ore-separators are also said to be used on a practical scale.

In conclusion I may mention that M. Heusler, of the Isabellenhütte, Dillenburg, kindly sent me an alloy which he defined as follows:—93–93·5 per cent. Mn, 1–1·2 per cent. Fe, ·2–·5 per cent. Si, and carbon. This gave not the slightest trace of an attraction by the pole of a steel magnet or of the Ruhmkorff, whether in a piece or pounded almost to dust.

I beg to tender my best thanks to Prof. F. Kohlrausch, in whose laboratory these experiments were carried out.

Phys. Inst. of Strasburg Univ.,
Nov. 1, 1889.

XXXIII. *An Improved Method of Determining Moisture and Carbonic Acid in Air.* By J. S. HALDANE, M.A., M.D., and M. S. PEMBREY, B.A., *Fell Exhibitioner of Christ Church, Oxford.* (From the Physiological Laboratory, Oxford.)*

WE were originally led to undertake the present investigation by difficulties experienced in measuring the respiratory exchange of oxygen and carbonic acid in animals. In the method which we wished to employ the results depend on an accurate determination of the difference in the percentage of moisture and carbonic acid in the air entering and that leaving a ventilated chamber in which the animal is placed. As the ventilation current is large, the difference to be measured is a small one, and errors of analysis are correspondingly important, especially in short experiments.

Although the object of our work was thus originally physiological, we have been guided chiefly by regard to the wider applications, particularly in meteorology, of the methods in question.

I. *The Determination of Moisture.*

Of the various methods in use for determining moisture in air the “chemical” method is generally acknowledged to be the most accurate when properly carried out. This method consists in the aspiration of a known volume of the air through one or more weighed tubes filled with a substance which absorbs moisture, such as anhydrous phosphoric acid or pumice soaked in sulphuric acid. The increase in weight of the absorption-tubes gives the weight of moisture contained in the air. The great disadvantage of this method as used

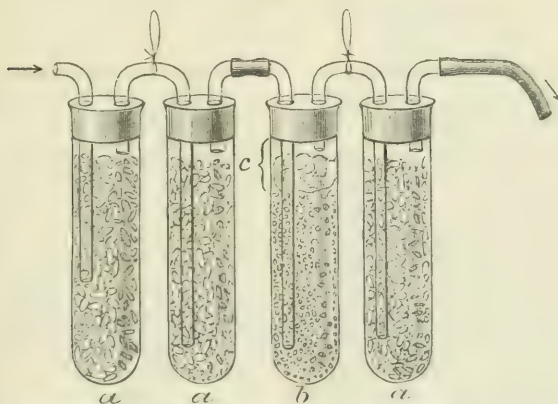
* Communicated by Prof. Odling, F.R.S.

hitherto lies in the fact that for an accurate analysis a very long period of experiment is necessary. The changes in the amount of moisture which in ordinary cases occur during the period of experiment are thus not indicated, and the method is rendered useless for many purposes, besides being very inconvenient.

The details of the method have recently been reinvestigated by Shaw, in a research undertaken at the request of the Meteorological Council*. He found that with a U-tube filled with pumice and sulphuric acid and weighing about 170 grammes, the absorption was complete with a rate of aspiration of about 8 or 10 litres per hour†. With double this rate there was a considerable escape of moisture through the first absorption-tube‡. Thus, with the faster rate of aspiration, the increase of weight of a second absorption-tube had to be added to the result. But since it was found that between the weighings the second tube frequently varied considerably in weight from accidental causes, the advantages of the faster rate were neutralized.

We have endeavoured to improve the method in three directions:—(1) by reducing to a minimum accidental variations in the weight of the tubes; (2) by increasing the efficiency of the absorbing tubes, and thus making a very rapid rate of aspiration possible; and (3) by making the apparatus more convenient.

Fig. 1.



Absorption apparatus for Moisture and Carbonic Acid, $\times \frac{1}{2}$.
a. Tubes filled with pumice soaked in sulphuric acid. *b.* Tube filled with soda-lime. *c.* Plug of cotton wool.

The absorption apparatus which we finally adopted is shown in fig. 1. We shall describe it in detail because, as will be

* Phil. Trans. vol. A, 1888, p. 73. † *Ibid.* p. 84. ‡ *Ibid.* p. 88.

seen below, the disadvantages of the chemical method, as ordinarily used, are dependent on a want of attention to details. It consists of a pair of test-tubes, containing pumice soaked in sulphuric acid. The test-tubes are 4×1 inch, and made of thin glass. Each tube is provided with a double-bored cork about $\frac{1}{2}$ inch thick, which is fitted with glass tubing of about $\frac{3}{16}$ inch internal diameter, and in the form shown in the figure*. The tubing must fit firmly. The corks are covered with a layer of hard paraffin inside and out. They are pushed down a very little below the tops of the tubes, the end of each tube being first wiped inside free of acid, and then warmed to soften the paraffin on the cork and so facilitate its entrance. To enable the longer limb of the tubing to be pushed down, a passage should first be cleared in the pumice with a piece of glass rod. A layer of paraffin is spread smoothly over the top of the cork until it is just level with the edges of the tube. The apparatus must be absolutely tight, and should allow air to pass perfectly freely when suction is applied. It should finally be carefully cleaned with a wet cloth to remove any traces of acid, and then dried.

The pumice is sifted through a wire sieve with about 7 meshes to the inch, and shaken in a fine one to remove the powder. It is then heated to redness by playing on it with a large blowpipe-flame, and thrown still hot into "pure redistilled" sulphuric acid. The superfluous acid is then poured off, and the pumice preserved for use in a stoppered bottle. Before using the tubes for experiments we have always taken the precaution of washing them out with air, as the air passed through them at first usually tastes slightly of sulphurous acid.

Each pair of tubes when filled weighs about 80 grammes, and can therefore be weighed on any ordinary balance.

To diminish to a minimum errors arising from accidental variations in weight of the tubes, we adopted the plan of weighing against a counterpoise consisting of a similar absorption-tube, and of about the same weight. This counterpoise is always kept in the same place as the absorption-tubes. Since during an experiment the absorption-tubes will

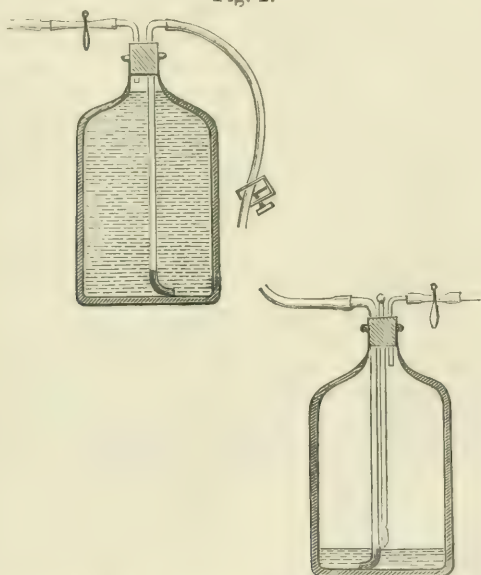
* The longer piece of glass tubing in the first sulphuric acid absorption-tube is made somewhat shorter than the corresponding tubing in the other absorption-tube. The inconvenience arising from the collection of water in the first tube is thus avoided.

Since writing the above we have been supplied by Messrs. Gallenkamp with pairs of tubes made in one piece. These are more brittle, but otherwise very convenient.

have been warmed above the temperature of the counterpoise, the weighing must be deferred for half an hour, so as to allow their temperatures to become equal again. The tubes are weighed unstoppered. If several tubes are to be weighed the stoppers* are removed before weighing from the whole of the tubes, including the counterpoise, and not replaced until the last tube has been weighed. No absorbent is kept inside the balance-case. The tubes should be lifted by the wires attached to them for hanging on the balance.

We found the following form of aspirator very convenient, especially when the apparatus had to be carried to a distance. Two bottles (fig. 2), each holding about 3200 cub. cent. up to a mark in the neck, were arranged as shown in the figure, and connected together by a piece of stout, non-collapsing rubber-

Fig. 2.



tubing provided with a screw-clip for regulating the rate of aspiration. The burette clips are for starting or stopping the flow. The bottles are covered outside with a layer of felt, to keep the temperature of the air and water equal during an experiment, and also to prevent breakage. A vertical strip on each bottle is, however, left uncovered, so that the height of the water may be watched during the experiment and the

* The stoppers used are the ordinary ones, consisting of a short piece of black rubber about $\frac{3}{4}$ inch long, closed at one end by a piece of glass rod.

reading of the thermometer taken. It is convenient to graduate the bottles roughly by pasting strips of paper at intervals of half a litre up the uncovered strip of glass. With the help of this graduation it is easy to ascertain if the aspirator is running at about the proper rate.

To graduate the aspirator, one of the bottles is allowed to drain for a minute, and is then weighed accurately. The two bottles are now connected and the weighed bottle is filled with distilled water to the mark, the tubing also being filled with water. The cork of the weighed bottle is then removed, care being taken to let no water escape from the end of the long piece of glass tubing. The bottle filled with water is then weighed again; and by deducting this weight from that of the empty bottle and allowing for air displaced &c., as in the graduation of a measuring-flask, the amount of water held by the bottle filled to the mark with the tubing in it, is obtained. The difference between this amount and some round number of cub. cent., such as 3000, is then measured into the bottle, which has been previously emptied and drained for a minute. The cork is then replaced, care being taken, as before, not to spill any of the water in the tubing. The aspirator is now ready for use, and measures off with the utmost exactness 3000 cub. cent. of air each time it is reversed.

We are now in a position to consider the advantages of the method as thus modified. As regards, firstly, errors of weighing, we found, in accordance with previous observers, that an absorption-tube, when left to itself, varies considerably in weight from hour to hour. The same is true of a tube through which dry air from another absorption-tube is passed*. There is usually a gain in weight, but sometimes a loss. This may be due partly to variations in temperature and barometric pressure. It is also due to gradual penetration of moisture into the tubes and to the varying amount of moisture deposited on the surface of the glass. The amount of this variation in weight was often two milligrammes or more, both in Shaw's experiments and our earlier ones with other absorption-tubes. With the method just described the tubes did not vary in apparent weight by more than three decimilligrammes in a day; and these slight variations were in part accounted for by small imperfections in our set of weights.

The advantages of using a counterpoise are illustrated by an experiment in which weighings with the counterpoise were compared at intervals with ordinary weighings during

* Cf. the data on this point given by Shaw, *loc. cit.* p. 84.

several days. The differences found are shown in the following Table:—

Intervals between weighings.		20 hours.	3 hours.	4½ hours.	42 hours.
Counter- poise tube	Ordinary (66·9230 grms.)	+0·0012	+0·0010	+0·0008	+0·0024
	Ordinary (77·7075)	+0·0009	+0·0008	+0·0018
Tube 1	Comparative..... (10·7840)	±0·0000	±0·0000	-0·0004
	Ordinary (87·6274)	+0·0007	+0·0015	+0·0023
Tube 2	Comparative..... (20·7041)	-0·0001	+0·0002	+0·0002
	Ordinary (69·6367)	+0·0009	+0·0010	+0·0006	+0·0018
Tube 3	Comparative..... (2·7136)	±0·0000	-0·0002	±0·0000	-0·0005

With regard, secondly, to the rate of aspiration possible and the lasting powers of the tubes, we made a number of experiments.

When a single absorption-tube was used, instead of the double ones described above, the absorption in the first tube was perfect (at least with rates up to two litres per minute) for a considerable time, as shown by the following experiments.

Experiment No. 1.

90 litres of air were aspirated at a rate of 1 litre per minute through two single absorption-tubes connected together by a very short piece of rubber tubing. The aspirator in this and the following experiment was a glass filter-pump, the air being measured by a gas meter:—

Tube 1 +0·5142.
Tube 2 +0·0000.

Experiment No. 2.

90 litres aspirated at 1 litre per minute.

Tube 1 +0·4712.
Tube 2 +0·0002.

Experiment No. 3.

50 litres aspirated at 1½ litres per minute.

Tube 1 +0·4057.
Tube 2 +0·0001.

Experiment No. 4.

21 litres aspirated at 2 litres per minute.

Tube 1 +0.2334.

Tube 2 +0.0000.

Experiment No. 5.

50 litres aspirated at 1 litre per minute.

Tube 1 +0.4163.

Tube 2 -0.0003.

The same tubes were not used through all these experiments, as tube No. 1 had become spent in the middle of the series. The use of double tubes enormously increases the lasting powers, so that, as shown by the following experiment, a double tube may be used for 300 determinations or more without being recharged.

Experiment No. 6.

The number of analyses possible without refilling a double absorption-tube was determined by aspirating air through two of them at a rate of 1 litre a minute, and weighing the second pair at intervals. 120 litres had previously passed through pair No. 1.

Litres of Air Aspirated through Pair 1.	Variation in Weight of Pair 2.
235	-0.0005 *
354	-0.0002
418	+0.0000
568	-0.0001
753	-0.0003
1046	+0.0000
1225	
1346	+0.0001
1588	+0.0003
1767	-0.0002
1994	+0.0000
2200	-0.0001

At the end of the experiment the first pair had absorbed 12.8255 grammes from 2320 litres of air. Although this pair was still absorbing moisture completely we did not continue the experiment further, on account of the inconvenient accumulation of dilute acid in the first tube.

As in determining moisture we have generally made a carbonic-acid determination simultaneously, our usual rate of

* Weighed by mistake five minutes after experiment.

aspiration has (for reasons given, p. 321) been about 1 litre per minute. The following were test experiments with faster rates :—

Experiment No. 7.

25 litres aspirated at 3 litres per minute.

Pair (1)	+0.2012.
Pair (2)	+0.0004.

Experiment No. 8.

25 litres aspirated at 4 litres per minute.

Pair (1)	+0.3453.
Pair (2)	+0.0003.

Experiment No. 9.

21 litres aspirated at 7 litres per minute.

Pair (1)	+0.2142.
Pair (2)	+0.0001.

The rate of aspiration may thus be, if required, 7 litres per minute.

With the view of determining whether there is any appreciable constant error due to incomplete absorption of moisture by the first tube, we have added up the variations in weight of the second tube in all our experiments in which a second absorption-tube was used.

Total moisture absorbed
by first tube.

13.0522 grms.

Sum of variations
of second tube.

—0.0007 grms.

The mean variation in weight of the second tube was thus only 0.0065 per cent. ; and a constant error of this order would be quite inappreciable in ordinary experiments.

Additional evidence of the accuracy of the method is afforded by the fact that in the simultaneous determinations recorded below (pp. 322 and 327) the two sets of results are practically identical. We have also made for another purpose two experiments in which air dried by sulphuric acid was passed through a weighed vessel containing water, and then again through a drying apparatus. The apparatus used was on a much larger scale, and the rate of aspiration was in one case 7 and in the other 15 litres per minute. The balance employed weighed to centigrammes. The vessel containing water lost 4.86 and 3.62 grammes, and the drying vessels gained 4.86 and 3.61 grammes respectively.

If the modified method described above be compared with the old method as investigated by Shaw, it is seen that by the

modified method the rate of aspiration may be more than 20 times as fast and the accidental errors in weighing are reduced to a sixth or less. Thus for a given duration of experiment the error in the modified method is less than a hundredth of that by the older method. In other words, an experiment of one minute's duration by the modified method is equal in accuracy to a two hours' experiment by the older method.

It is perhaps hardly necessary to refer to the great convenience of the modified method. For experiments in the open air sets of weighed tubes can be carried even for long distances in a box with places arranged for the tubes. We have found that no variation in weight is caused by the shaking, &c. (see p. 317). No precautions beyond the very simple ones above mentioned are necessary in weighing; and with a good short-beam balance not more than three minutes are occupied in the whole of the manipulations connected with weighing. Once an absorption-apparatus is filled it is always ready for use, and may be used every day for nearly a year. The fact that only a small quantity (usually about 6 litres) of air is needed for an analysis makes it possible to use an easily portable aspirator, such as that described above.

II. *Comparative Experiments with the Dry- and Wet-Bulb Psychrometer and the Apparatus described above. (Made at the Radcliffe Observatory, Oxford, by M. S. P.)*

This series of experiments was undertaken with a view to test the degree of accuracy attainable by ordinary observations with the dry- and wet-bulb psychrometer; and also with the object of obtaining independent evidence as to the accuracy of the different tables used in connexion with the psychrometer.

The chemical method has been recognized by Regnault and others as the standard with which to compare all other hygrometers. How important the first of these observers considered the method is shown by the following extracts from his *Etudes sur l'Hygrométrie*:—" . . . j'attachais un grand intérêt à rendre cette méthode éminemment pratique et facile à employer dans toutes les expériences hygrométriques."*

"La méthode chimique convient éminemment à la vérification des autres méthodes hygrométriques et à la détermination des constantes numériques que plusieurs d'entre elles exigent. J'en ai constamment fait usage, à ce point de vue, dans les recherches qui font l'objet de mon premier Mémoire."†

* *Annales de Chimie et de Physique*, xv. p. 152 (1845).

† *Ibid.* xxxvii. p. 257 (1853).

Although Regnault proved by experiment that the absorption of moisture was complete with the chemical method, yet he was prevented from bringing it into general use in hygrometry by two difficulties. These were the inaccuracy of the weighings, and the slow rate at which the air could be aspirated through the absorption-tubes*. All other observers who have used the chemical method have had to encounter these same difficulties. Even the mercury-joints and glass-stoppered absorption-tubes used by Shaw have not removed the errors arising from these causes†. Each determination made by these observers required about one hour, and generally longer. By what simple means these serious errors can be avoided has been shown above.

I must here express my hearty thanks to the Radcliffe Observer for giving me every facility to carry out these experiments. To his assistants Messrs. Wickham, Robinson, and Bellamy, my thanks are also due.

Two determinations were made each time and as nearly simultaneously as possible. Two aspirators similar to the one described above were used. Four pairs of absorption-tubes were employed each time:—pair 1 for determination A; pair 2 for determination B; pair 3 as a test pair to show if any alteration in weight was caused by carrying the tubes from the Physiological Laboratory (where the tubes were weighed) to the Radcliffe Observatory and back; whilst pair 4 was the counterpoise.

The tubes were carried in a small box with partitions of copper wire to prevent them from knocking against each other. The entrance tube, by which the air to be examined passed into the pair 1 (or 2), was fixed through a small perforation in a rubber partition covering a hole in the box, so that there was no possibility of air being taken from the inside of the box. The box and its tubes were placed about 1 foot below the wet and dry bulbs. That the air in this position might be fairly compared with that in the shed containing the psychrometer is shown by experiment 6, in which pair 2 was placed in the shed close to the bulbs, and pair 1 in the usual place below.

In making a determination the following was the order of

* *Ann. de Chim. et de Phys.* xv. pp. 153 and 164. “La méthode chimique est trop embarrassant, et elle exige une manipulation trop longue pour qu’on puisse l’employer souvent dans les observations météorologiques.”

† Shaw on Hygrometric Methods, *Phil. Trans.* 1888, A, pp. 83 and 84. The variations in weight range from -0.0009 to $+0.0023$ gram, or still higher.

procedure. The wet and dry bulbs were first read off; the absorption-tubes, pairs 1 and 2, were then connected by two long pieces of rubber tubing with their respective aspirators, and the air was drawn through them at as equal a rate as possible. The readings of the thermometers in the aspirators were now taken. When one known volume (2900 cub. cent.) had been drawn through, the aspirators were quickly reversed and started again until 5800 cub. cent. of the air had been taken for each determination. The thermometers in the aspirators were now again read; the readings of the wet and dry bulbs entered; the apparatus disconnected; and the absorption pairs 1 and 2 stoppered. Everything was easily done in twelve minutes, whilst the actual period of aspiration was only about half this time, as shown by the Table of experiments.

How closely the two determinations agree Table I. will show, and there is no doubt that could they have been strictly simultaneous the agreement would have been still closer. This is well shown by a comparison of the first five or six experiments with the last four, in which the determinations were almost exactly simultaneous.

To show that no practical error was introduced in the weighings by carrying the tubes about, the variation of the test pair 3 is given in Table I.

In calculating the results for the psychrometer in Table I. I have taken the mean of three readings—one at the beginning, one at the middle, and one at the end of each period of aspiration (*i. e.* one reading about every two minutes). These readings were obtained from a continuous photographic record of the wet and dry bulb taken at the Radcliffe Observatory. This record can be read off to two minutes and one tenth of a degree Fahrenheit, and its accuracy has been proved by years of use and comparison with eye-readings. The volume of air drawn through the tubes has always been corrected for temperature, aqueous vapour, and barometric height. In calculating the tension of aqueous vapour from the chemical determinations I have used the table given by Shaw in his paper on Hygrometric Methods*.

The mean of all these gravimetric determinations compared with the mean of the amounts of moisture calculated from the psychrometric readings is .0551 to .0549 grm., or less than $+\frac{1}{2}$ per cent. Thus although the psychrometric result varied from the standard chemical method in the above series by + 6 per cent. to - 5 per cent., the mean difference is insensible.

* Phil. Trans. 1888, A, pp. 78, 79.

TABLE I.

Experiment.	Date.	Time during which air was aspirated.	Corrected volume of air aspirated through each pair.	Gain in weight of pair 1, determined	Gain in weight of pair 2, determined	Weight of vapour calculated from readings of psychrometer by Glaisher's Tables, 7th ed.	Percentage difference of meter over chemical method.	Dry bulb (mean of 3 readings).	Wet bulb (mean of 3 readings).	Variations of test pair 3, showing the tubes about introduced no error of weighing.
1.	16 July 1889	11.30-11.48 A.M.	cub. centim. 5723	gram. +0.21	gram. +0.30*	gram. +0.450	per cent. +5.3 $\frac{1}{2}$	61.6°	53.0°	gram. +0.001
2.	17 "	11.30-11.45 A.M.	5722	+0.29	+0.24	+0.52	+5	58.3	54.5	+0.002
3.	18 "	11.10-11.16 A.M.	5723	+0.16	+0.12	+0.20	+1	61.3	54.9	-0.002
4.	19 "	11.6-11.12 A.M.	5780	+0.502	+0.508	+0.519	+3	63.7	56.0	+0.002
5.	20 "	11.45-11.52 A.M.	5681	+0.613	+0.610	+0.600	-2	57.9	56.0	+0.003
6.	22 "	12.13-12.16 P.M.	5732	+0.440	+0.435	+0.452	+3	61.5	53.0	-0.002
7.	5 Aug. 1889	11.52-11.58 A.M.	5707	+0.87	+0.668	-3	65.6	60.7	-0.003
8.	6 "	11.48-11.54 A.M.	5709	+0.64	+0.548	-3	62.5	56.5	±0.000
9.	7 "	11.21-11.27 A.M.	5736	+0.510	+0.510	+0.495	-3	63.0	55.2	+0.002
10.	8 "	11.0-11.7 A.M.	5776	+0.75	+0.72	+0.552	-4	64.1	57.0	+0.001
11.	9 "	11.24-11.30 A.M.	5731	+0.78	+0.75	+0.678	±0	61.0	58.9	+0.002
12.	10 "	11.32-11.39 A.M.	5755	+0.83	+0.85	+0.53	-5	64.6	57.4	-0.001

* The rubber of one of the stoppers was found to be split on reaching the Observatory, and this accounts for the slight excess in weight of this pair of tubes.

During some experiments the psychrometer was very steady; at other times it showed considerable fluctuations. As examples may be given the readings of the wet and dry bulbs for the experiments 1 and 5.

Exp. 1.	Dry.	Wet.	Exp. 2.	Dry.	Wet.
11.39 A.M.	61.4	52.9	11.45 A.M.	57.9	55.9
11.43	61.8	53.1	11.49	57.9	56.0
11.47	61.6	52.9	11.52	58.0	56.0

It is to be noticed that a difference of two or three tenths of a degree Fahrenheit in the reading alters greatly the percentage error.

I have also calculated out the tension given by the chemical method, and have compared it with the results calculated from the psychrometer by means of Glaisher's, Haeghen's, Guyot's, and Wild's Tables.

TABLE II.

Experiment.	Chemical Method.	Psychrometer.			
		Glaisher.	Haeghens.	Guyot.	Wild.
	mm.				
1	7.43	7.76	7.37	7.31	7.4
2	9.15	9.55	9.54	9.51	9.5
3	8.99	9.00	8.88	8.87	8.9
4	8.78	8.99	8.74	8.77	8.8
5	10.70	10.72	10.75	10.76	10.7
6	7.63	7.78	7.39	7.34	7.4
7	12.15	11.72	11.78	11.80	11.7
8	9.91	9.65	9.57	9.57	9.6
9	8.90	8.68	8.45	8.43	8.5
10	10.00	9.52	9.38	9.41	9.4
11	11.82	11.84	11.93	11.93	11.9
12	10.23	9.67	9.55	9.57	9.5
Mean	9.64	9.57	9.44	9.44	9.44

This Table shows that Glaisher's Tables are the most correct as far as my experiments go. These tables were prepared by Glaisher from the Greenwich factors and Regnault's Table of pressures, and are in general use in England. Haeghen's Tables, which are used in France and Italy, Guyot's, which are almost identical with the last and are employed in America, and Wild's, which have been adopted

by Germany and Russia, are all reduced from Regnault's table of pressure and psychrometric formulæ.

In conclusion may be given the results obtained by other observers, who have compared the psychrometer with the chemical method. Regnault*, who made 106 experiments under very varied conditions, obtained for the mean percentage error 2, whilst the extreme percentage error varied from + 12 to - 10. In order to calculate out the results from the readings of the dry and wet bulbs, Regnault determined the values for the constant A in each series of experiments. Each experiment lasted about one hour; the readings of the psychrometer were taken every five minutes, and from the mean of these the result was calculated. M. Izarn made 34 comparative experiments in the Pyrenees. These are given by Regnault in his paper†. The extreme percentage differences are + 2 and - 3 in the first series, and + 10 and - 10 in the second.

Shaw made comparisons in a room with a current of air passing over the instruments; he does not, however, consider them satisfactory. The tensions calculated from the psychrometer by Glaisher's Tables were generally higher than those given by the chemical determination, the variations ranging from + 30 per cent. to - 7 per cent.‡.

III. *The Determination of Carbonic Acid.*

The method adopted by us for carbonic acid is similar in principle to that for moisture. The absorption-apparatus (see fig. 1) consists of a pair of test-tubes arranged in the same way as was described above (p. 307) §. The first tube is filled with soda-lime, and the second with sulphuric acid and pumice. The air must arrive perfectly dry at the absorption-tube for carbonic acid, and is therefore passed through the previously described absorption-apparatus for moisture. The connecting piece of rubber tubing should be as short as possible.

The soda-lime we have hitherto used was made by heating together in a copper vessel 1200 grms. of caustic soda in strong solution, and the product obtained by slaking to a fine powder 1000 grms. of quicklime. The heating was continued until the soda-lime became capable of being broken up into fragments in a mortar. The fragments were rapidly sifted

* *Annales de Chimie*, xxxvii. pp. 264-285 (1835).

† *Ibid.* pp. 275-272.

‡ *Phil. Trans.* 1888, A, p. 111.

§ The same counterpoise is used for the carbonic acid as for the moisture determinations.

in a wire sieve with about 12 meshes to the inch, and the product freed from powder by a finer sieve. We have also tried commercial soda-lime similarly sifted, and found that it absorbed CO_2 well (see p. 321). As a precaution against blocking of the tubing by soda-lime during the process of fitting, a small plug may be placed in the end of the tube and afterwards be withdrawn by a string attached to it. The figure shows that a piece of cotton-wool is placed between the surface of the soda-lime and the cork; the object of this is to prevent soda-lime being carried over in the form of powder by a rapid air-current.

The method was tested in the same way as that for moisture. As regards accidental errors of weighing, what was said above with regard to the apparatus for moisture applies equally to that for carbonic acid. With respect to the efficiency of the absorption, we may first quote the results of two experiments in which the soda-lime and sulphuric-acid tubes were weighed separately. In the subsequent experiments the double absorption-tubes just described were employed.

Experiment No. 1.

The tubes were arranged in the following order;—1 and 2, sulphuric acid; 3, soda-lime; 4, sulphuric acid; 5, soda-lime; 6, sulphuric acid. 90 litres aspirated at a rate of 1 litre per minute.

Tube 3	.	.	+0.0463	} together	+0.0868.
„ 4	.	.	+0.0405		
„ 5	.	.	−0.0221	} together	−0.0001.
„ 6	.	.	+0.0220		

Experiment No. 2.

Repetition of No. 1; 90 litres aspirated at a rate of 1 litre per minute.

Tube 3	.	.	+0.0360	} +0.1198.
„ 4	.	.	+0.0838	
„ 5	.	.	−0.0828	} +0.0004.
„ 6	.	.	+0.0832	

Experiment No. 3.

90 litres aspirated at a rate of 1 litre per minute.

Soda-lime, pair 1	.	.	+0.1615.
„ „ 2	.	.	+0.0001.

Experiment No. 4.

50 litres aspirated at a rate of $1\frac{3}{4}$ litres per minute.

Soda-lime, pair 1	. .	+0.0558.
„ „ 2	. .	+0.0001.

Experiment No. 5.

21 litres aspirated at a rate of 2 litres per minute.

Soda-lime, pair 1	. .	+0.0339.
„ „ 2	. .	+0.0003.

Experiment No. 6.

In this experiment commercial soda-lime (Hopkins and Williams) was used.

The soda-lime contained much more water than ours, as shown by its appearance and the amount of water it gave up to dry air. 50 litres aspirated at a rate of 1 litre per minute.

Soda-lime, tube 1	-0.0552	} together	+0.0371.
Sulphuric acid, tube 3	+0.0923		
Soda-lime, pair 2	+0.0000.		

Experiment No. 7.

The same soda-lime tube was used as in the previous experiment. 50 litres aspirated at a rate of 2 litres per minute.

Soda-lime, tube 1	-0.0478	} +0.0415.
Sulphuric acid, tube 3	+0.0893	
Soda-lime, pair 2	+0.0013.	

A rate of 1 litre a minute is thus well within the limit of safety, so that even should the aspiration be temporarily faster, there is no risk of appreciable non-absorption of either moisture or carbonic acid.

The number of analyses possible without refilling the carbonic-acid tubes was determined in the same way as for the moisture-tubes, *i. e.* by passing air through two pairs at a rate of 1 litre per minute, and weighing the second tube at intervals.

Experiment No. 8.

120 litres of air had already been passed through pair No. 1.

Litres of air aspirated through pair 1.	Variation in weight of pair 2.
235	+0.0003
354	-0.0001
418	+0.0010
568	+0.0049

At the end of the experiment pair No. 1 had absorbed 0·4371 gram of carbonic acid from 688 litres of air. We concluded that 500 litres of air might be safely passed through an absorption-apparatus. Other experiments confirmed this conclusion.

The mean error of the method for carbonic acid was estimated in the same way as with the method for moisture (p. 311).

Total CO ₂ absorbed by tubes No. 1 . . .	0·6464
Sum of variations of tubes No. 2 . . .	+0·0007

The mean error was thus about 0·1 per cent.

The method is thus exceedingly accurate, in this respect far exceeding, as will be shown below, the other methods in common use.

For free air about 20 litres or more, according to the accuracy aimed at, will be required for an analysis. For vitiated air, such as that of schools, 3 to 6 litres will suffice.

The result of a pair of simultaneous experiments made out of doors may be quoted here. 18 litres of air were aspirated in each case.

No. 1.

Sulphuric acid pair	+0·0820
Soda-lime pair	+0·0109

No. 2.

Sulphuric acid pair	+0·0819
Soda-lime pair	+0·0109

The methods just described have now been in use in this laboratory for nearly a year. They have also been used for some months in experiments out of doors at the Radcliffe Observatory here, and in the country in Scotland. So far as our own experience of them goes they have successfully stood the test of every-day use.

We may now review shortly the literature bearing on the determination of carbonic acid in air, and record some experiments which we made with a view to testing the two methods at present in common use in this country.

The first attempt at a quantitative analysis of the carbonic acid in free air seems to have been made by A. von Humboldt*. His numerous results were, curiously enough, entirely illusory, since he concluded that about 100 vols. per 10,000 of air were usually present. In 1802 Dalton†, who

* Gilbert's *Annalen*, iii. p. 79 (1800).

† Manchester Lit. Phil. Soc. Mem. 1802.

made the first approximately correct analyses, reduced the amount to 6·8 vols. ; and De Saussure * had, about 1830, brought it down to a mean of about 4·1 vols. for country air. This result was confirmed by Watson (1834) and Boussingault (1844), who used other methods, and for long was supposed to be nearly correct. Still more recent researches, particularly those of Angus Smith † in Scotland, Schultze in Germany, Reiset ‡ in France, and Müntz and Aubin in France§ and other countries, have gradually reduced it by about a third more.

There still, however, exists a considerable amount of apparent contradiction on the subject. Not only are the mean results of different observers different, but there is perhaps still greater want of agreement as regards the limits within which the proportion of CO_2 varies. That the uncertainty and want of agreement which prevails is probably due to the imperfection of some, at least, of the methods employed will, we believe, be evident from the experiments to be recorded below. The subject of the variations in the carbonic acid of free air will, however, be taken up in a future paper.

The methods at present in use for the determination of carbonic acid in air are, practically speaking, of two kinds : (1) those in which the CO_2 is absorbed by standardized baryta-water, which is afterwards retitrated ; (2) those in which it is absorbed by potash, and afterwards liberated by acid and measured in the form of gas||.

The method best known in this country is that of Pettenkofer¶, or, more correctly, of Dalton** and Pettenkofer. In this method a large bottle is pumped full of the air to be examined. A measured quantity of standardized baryta-

* *Annales de Chimie*, xliv. p. 5.

† 'Air and Rain,' p. 59.

‡ *Annales de Chimie*, xxvi. p. 145 (1882).

§ *Ibid.* xxvi. p. 222 (1882), xxx. p. 238 (1883).

|| A valuable critical account of the methods hitherto used is given by Blochmann, *Liebig's Annalen*, cxxxvii. p. 39 (1887).

¶ *Abhandl. der techn. Commission der Bayer. Akad.* ii. p. 3 (1858) ; and *Liebig's Annalen*, Suppl. ii. p. 23 (1861).

** The form finally given to Dalton's method is described in a paper by Watson, communicated by Dalton to the British Association (*Brit. Assoc. Report*, 1834, p. 583). Watson used a large bottle, which he filled with air with the help of a pair of bellows. He then added lime-water, and after shaking allowed the bottle to stand for several days, at the end of which time he filtered off the carbonate, and titrated with dilute sulphuric acid. Pettenkofer independently invented a similar but improved method. He introduced baryta-water as an absorbent, and turmeric as an indicator, and avoided the filtration. Watson's mean result for country air (4·1 vols.) was about the same as that obtained by the earlier observers who used Pettenkofer's method.

water is then added, and the bottle closed and shaken, so as to bring the air in contact with the baryta. After a certain time the baryta solution is again titrated, and the CO_2 estimated from the loss of alkalinity of the baryta-water.

For certain cases where the bottle method is not suitable, Pettenkofer recommends that a measured quantity of air should be allowed to bubble through a long tube placed nearly horizontally, and containing a known quantity of baryta-water. The CO_2 absorbed by the baryta is estimated in the same way as in the first method. Pettenkofer found that about 5 litres per hour is the maximum rate at which the air can be passed.

Reiset* has recently devised an apparatus which allows large quantities of air to be aspirated through baryta-water. With this apparatus he was able to aspirate as much as 100 litres through 300 cub. cent. of baryta-water in an hour. The absorption of CO_2 appears to have been complete. Each experiment lasted several hours. He used an enormous aspirator, mounted on a cart, and capable of holding 600 litres of water.

The method in which the CO_2 is absorbed by potash, and afterwards liberated by acid and measured in the form of gas, was in its first form used by Mangon and Tissandier† for balloon experiments. A rough form of this method has been for some years in use at the Paris Observatory. The method has been brought to great perfection by Müntz and Aubin‡, whose test-experiments show that an accuracy to about 2 per cent. of the CO_2 estimated may be attained when 200 litres of air are used. For absorbing the CO_2 they use tubes about a metre long, filled with pumice soaked in caustic-potash solution free from CO_2 . After the experiment the CO_2 is liberated by the addition of acid, and collected over mercury with the help of a mercury-pump. The apparatus and manipulations required are very complicated, so that the method is not likely to come into general use. Müntz and Aubin confirmed and extended Reiset's conclusions, and found that the mean proportion of CO_2 in country air is about 2.85 vols. per 10,000, and that it very seldom rises above 3.1 or falls below 2.6. The experiments of these three observers are certainly the most reliable of any hitherto published.

Gravimetric methods of determining CO_2 in air were at one time much employed, although they have been practically disused since the introduction of Pettenkofer's method. In

* *Loc. cit.* p. 164.

† *Comptes Rendus*, lxxx. p. 976 (1875).

‡ *Annales de Chimie*, xxvi. p. 222 (1882).

1832 Brunner* described a gravimetric method. He aspirated the air at a rate of about 30 litres an hour through two absorption-tubes. The first contained asbestos soaked in sulphuric acid; and the second, which was 3 feet long, was filled in the first two thirds with moist slaked lime, and in the last third with sulphuric acid and asbestos. He tested the completeness of the absorption of the CO_2 by allowing the air to bubble afterwards through baryta-solution, which remained clear. The increase in weight of the first tube gave the moisture, that of the second the CO_2 in the air aspirated. He says he always obtained for free air results lying between De Saussure's maximum and minimum (3.7 and 6.2 vols. per 10,000).

Brunner's method, with various modifications, has been used by a number of subsequent observers. The most reliable results were those of Boussingault, who obtained with large volumes of air a mean of 4.0 vols. per 10,000 for Paris air†. The results of several other observers were certainly quite unreliable.

In 1856 Hlasiwetz‡ published a paper in which he criticised adversely the gravimetric method. He made a number of analyses by different forms of this method, and found that not only did analyses simultaneously made often entirely disagree, but that in eleven out of fifty-six analyses the absorption-apparatus for CO_2 actually lost in weight. These results he set down partly to unavoidable "errors of weighing," and partly to the fact that CO_2 is absorbed by sulphuric acid. Hlasiwetz's criticisms appear to have been generally accepted as conclusive; and since the publication of his paper the gravimetric method has been almost entirely given up, though still described in some text-books.

Soda-lime has for long been in use as an absorbent for CO_2 in combustions. It was first used by Mulder§ in 1859, and Fresenius|| has shown its superiority to potash-solution &c. Its successful use by one of us in a new form of animal-respiration apparatus¶ suggested the working out of the method described above.

We have made experiments with a view to testing by our

* *Annalen der Physique*, xxiv. p. 570.

† *Annales de Chimie*, x. p. 456 (1844).

‡ *Sitzber. der Wiener Akad. (Math.-nat. Kl.)* xx. p. 189.

§ *Zeitschr. für Anal. Chem.* i. p. 3.

|| *Ibid.* v. p. 89.

¶ A full account of this apparatus will shortly be published. A preliminary paper on the subject was published in the 'Proceedings of the Oxford University Junior Scientific Club' for October Term, 1888.

gravimetric method the bottle method and also the tube method of Pettenkofer.

The bottle method is in general use in this country and in Germany, and is in many ways exceedingly convenient. There are reasons, however, for suspecting that even in experienced hands it may give seriously inaccurate results for free air. Thus although the French experiments referred to above, and a series at present in progress by our own method, show that the real proportion of carbonic acid is, as a rule, under 3 vols. per 10,000, and fluctuates within pretty narrow limits; yet with the Pettenkofer method a very different average proportion is often obtained, and the apparent limits of fluctuation are, as a rule, much greater.

We may quote a few recent instances. Marcet and Landriset* found at two country stations near Geneva 2·7 to 4·9 vols. per 10,000, mean 3·76 vols. Carnelley, Haldane, and Anderson†, who titrated with the barium carbonate in suspension, found in the outskirts of Dundee and Perth 1·7 to 3·5 vols., mean 2·9. Feldt‡, who also titrated with the carbonate in suspension, found in Dorpat 1·85 to 3·65, mean 2·66 vols. The results of pairs of simultaneous analyses made by him sometimes disagreed by as much as 30 per cent. Uffelmann§, in Rostock, found a mean of 3·5 vols., whereas Schultze at the same place had previously obtained an average of 2·9 vols. Yet these three observers seem to have used very nearly the same modification of Pettenkofer's method. All titrated straight into the absorption-bottle, the carbonate being still in suspension.

In the following comparative experiments, which were nearly all made within doors, every care was taken to obtain the air from the same place in the room, and at the same time in each pair of determinations. The bottles were pumped full of air when the aspiration through the tubes was half over.

For the Pettenkofer analyses we used two large bottles of 10,680 and 10,800 cub. cent. capacity, with ground-glass stoppers ||. Before each analysis these bottles were washed, first with tap-water, and then with distilled water, and dried. They were not washed with acid. The air was pumped into the bottle with a bellows, 100 cub. cent. of baryta-water

* R. Meteorol. Soc. Journ. xiii. p. 167 (1887).

† Phil. Trans., B, 1887, pp. 66, 68.

‡ *Der Kohlensäuregehalt der Luft zu Dorpat*, 1887.

§ *Archiv für Hygiene*, viii. p. 252 (1888).

|| India-rubber caps are objected to by Blochmann, Liebig's *Annalen*, ccxxxvii. p. 39 (1887).

Gravimetric Method.					Pettenkofer Method.		
Number.	Litres of air aspirated.	Increase in weight of moisture pairs.	Increase of carbonic acid pairs.	Vols. of CO ₂ per 10,000.	Vols. of CO ₂ per 10,000.	Percentage excess over gravimetric result.	Percentage difference in double determinations.
1	12	0.0115	4.63	5.13	11 per cent.	
2	12	0.0108 *	4.35	4.67	7 "	
3	{ (a) 12 (b) 12	0.0020	0.0218	8.70	{ 9.30 } [†] 10.12	12 [†] "	
4	{ (a) 18 (b) 18	0.1045	0.0219	5.67	{ 6.42 6.49	14 "	1
5	{ (a) 18 (b) 18	0.1040	[0.0211 [†] 0.0175	4.74	{ 5.20 5.48	13 "	5
6	12	0.0176	3.17	{ 3.53 3.98	18 "	11
7	12	0.0079	3.33	{ 3.52 3.20	17 "	
8	18	0.0106	2.84	{ 2.48 2.49	18 "	9
9	18	0.0929	25.09	{ 2.47 2.90	-1 "	0
10	{ 2.91 3.10	2
11	{ 3.04 3.00	6
12	1

* A second carbonic acid pair used in this experiment and No. 3 (b) varied by +0.0001 and -0.0002 in the two experiments.
[†] The two Pettenkofer experiments were not quite simultaneous, and so cannot be compared together.
[‡] The aspirator leaked, and the volume aspirated had to be calculated from the moisture found.

added, and the bottle allowed to stand, with occasional shaking, for at least two hours. The baryta-water was then removed to a clean and dry cylinder, corked up, and titrated after the carbonate had subsided. We used as a rule either 30 or 40 cub. cent. of the baryta-water in the titration, which was performed twice with the ordinary oxalic-acid solution (1 cub. cent. = .001 gram. of CO_2), rosolic acid or phenolphthalëine being used as an indicator. The end reaction was always sharply defined, and the two results never differed by more than 0.1 cub. cent.

The above Table shows that with air containing a small proportion of carbonic acid the Pettenkofer method gave results from 8 to 27 per cent. higher than those given by the gravimetric method. As the proportion of carbonic acid rises (Experiment No. 9), the difference tends to disappear. Judging from these experiments the result for outside air would usually be about 15 or 20 per cent. too high by the bottle method.

It will be seen that the pairs of determinations made with the gravimetric method agree with the utmost closeness, both for moisture and carbonic acid.

We have not succeeded in tracing satisfactorily the reasons for the inaccuracy of our results with the bottle method. Although these results were all too high, other observers have, as before mentioned, obtained results which were often almost certainly too low.

We at first thought that the error might be due to contact of the baryta-water with air during the manipulations involved. In the first four or five analyses we had simply followed Pettenkofer's plan of pouring the baryta-water out of the large bottle through a funnel into the narrow vessel used for allowing the carbonate to settle. To avoid the exposure to air implied in this operation, we in the later experiments removed the baryta-water with a pipette provided with a piece of rubber tubing for applying suction. As the pipette was washed first with some of the baryta, it was free from carbonic acid. Our results, however, were little, if at all, better.

Another possible source of error is the state of the glass walls of the bottle. Pflüger* found in making the titrations for Kjeldahl nitrogen determinations that it was impossible to titrate accurately in flasks which had previously been washed with acid. The glass seemed to retain some of the acid in spite of washing, and give it up again slowly during the analysis. We made several experiments with a bottle

* Pflüger's *Archiv*, xxxvi. p. 105.

which had been washed with mineral acid and then allowed to stand full of water for a day; but the result was not always higher with this bottle.

In the bottle experiment No. 6 (*b*), which gives the worst result of all, a smaller bottle of about 3 litres capacity was used. In Parkes's '*Hygiene*,' 7th edition (1887), p. 711, it is stated that the results by the bottle method vary with the different sizes of bottle. It seems likely that as a rule the results will be less correct the smaller the bottle used.

When the results are too low this is as likely to be due to insufficient time being given for the carbonate to settle out as to incomplete absorption. If the attempt is made to titrate too soon, the result may be much too low, and the end reaction will be very indefinite.

It is no conclusive test of the correctness of the bottle method that two simultaneous experiments give the same result. If the conditions are kept the same in the two experiments, the results must be the same whether right or wrong. In the above experiments we usually varied the conditions somewhat as regards details supposed to be unessential. In experiments where the conditions were carefully kept the same, results were practically identical. There are doubtless several sources of error, which may neutralize one another more or less. The subject is complicated by the fact that nearly every observer introduces, often unconsciously, some new modification of the method.

We have come to the conclusion from the above experiments that the bottle method in its ordinary form is of very limited use for experiments on free air, though usually quite accurate enough in the case of vitiated air.

Blochmann* has recently described a modification of the bottle method which enables him both to avoid all possibility of contact of the baryta-water with air, and at the same time to titrate with perfectly clear baryta-water. For want of the special apparatus required we have not yet tested this method.

We used Pettenkofer's tube method in some of our earlier experiments for the purpose of testing the efficiency of the absorption of carbonic acid by soda-lime. Before we had overcome the difficulty caused by errors of weighing, we believed that any carbonic acid which had escaped absorption by the soda-lime would be indicated best by Pettenkofer tubes filled with baryta-water. Accordingly in different experiments the air was passed through one or more Pettenkofer tubes after it had passed through the soda-lime. We always found that the baryta-water had lost distinctly in alkali-

* Liebig's *Annalen*, cccxxvii. p. 72 (1887).

linity after the experiment. There were, however, several reasons for doubting whether this was really due to escape of carbonic acid through the soda-lime. We therefore made the following experiment.

A current of air, after passing through sulphuric acid and soda-lime absorption-tubes, was divided by means of T-tubes, and passed through six Pettenkofer tubes placed beside one another on a board. The loss of moisture from the baryta-water in these tubes was determined by means of a sulphuric acid absorption-tube placed in the air-current beyond them. The moisture which had collected in the tubing connecting the Pettenkofer tubes and this absorption-flask was washed into the flask by means of a current of dried air. 60 litres of air were aspirated in one hour.

In addition to the six Pettenkofer tubes through which the air was passed six others were taken, and charged with the same quantity of baryta solution in exactly the same way as the first set. These dummy tubes were kept stoppered during the experiment.

All the tubes were washed before the experiment, first with dilute nitric acid, then three times with tap-water, and finally with distilled water. At the end of the experiment the baryta from each set of tubes was poured into a small flask, and at once corked and allowed to stand for a time. During these manipulations every precaution was taken to avoid unnecessary contact of the baryta-water with air. The results are given in full.

Sulphuric acid, pair 1. +0.4183.

Soda-lime, pair 1. +0.0554.

Baryta-water from first set of Pettenkofer tubes. $\left\{ \begin{array}{l} (1) \text{ 40 c. c. } = 39.9 \text{ c. c. standard oxalic.} \\ (2) \text{ " } = 39.9 \text{ " " " " " } \end{array} \right.$

Loss of water from same tubes by evaporation 0.8408 gram.

Baryta-water from dummy set of Pettenkofer tubes. $\left\{ \begin{array}{l} (1) \text{ 40 c. c. } = 39.65 \text{ c. c. standard oxalic.} \\ (2) \text{ " } = 39.75 \text{ " " " " " } \end{array} \right.$
Mean . . 39.7

Standard baryta-water 40 c. c. = 40.25 standard oxalic.

Therefore

loss of alkalinity in 1st set = $6 \times 0.35 = 2.1$ c. c. standard oxalic
and loss by evaporation = $\frac{0.84}{2.94}$ " "

loss of alkalinity in 2nd set = $6 \times 0.55 = 3.3$ " "

The dummy tubes had thus actually lost slightly more in alkalinity than the tubes through which the air had passed. This loss is about equal to what would be caused by the absorption of the carbonic acid contained in 6 litres of pure air.

It follows from this and the other experiments just referred to that the error with the tube method may be considerable, at least in experiments of not more than two or three hours' duration.

XXXIV. *On the Structure of the Line-Spectra of the Chemical Elements.* By J. R. RYDBERG, Ph.D., Docent at the University of Lund*.

(PRELIMINARY NOTICE.)

THE researches, the most important results of which are given in the following pages, will be published with full details in the *Svenska Vetensk.-Akad. Handlingar Stockholm*. They have extended hitherto only to the elements which belong to the groups I., II., III. of the periodical system; there is, however, no reason to doubt but that the laws I have found can be applied in the same way to all elements.

In my calculations I have made use of the *wave-numbers* (n), instead of the wave-lengths (λ); $n = 10^8 \cdot \lambda^{-1}$, if λ be expressed in Ångström's units. As will be seen, these numbers will determine the number of waves on 1 centim. in air (760 millim., 16° C. according to Ångström), and are proportional, within the limits of the errors of observation, to the numbers of vibrations.

1. *The "long" lines of the spectra form doublets or triplets, in which the difference (ν) of wave-numbers of their corresponding components is a constant for each element.*

This law, found independently by the author, has already been announced by Mr. Hartley for Mg, Zn, Cd. The values of the constant differences (ν) vary from $\nu = 3.1$ in the spectrum of Be to $\nu = 7784.2$ in the spectrum of Tl. In each group of elements the value of ν increases in a somewhat quicker proportion than the square of the atomic weight. For instance:—

* Communicated by the Author.

Element ...	B.	Al.	Ga.	In.	Tl.
P	10.9	27.04	69.9	113.4	203.7
ν	10.5	109.6	823.6	2212.4	7784.2
$\frac{100\nu}{P^2}$	8.84	14.99	16.86	17.20	18.76

In accordance with analogy, the spectral lines of Li (the one element, besides H, in which only single lines are observed) ought to be double with $\nu=0.8$, corresponding, for instance, in the red line ($\lambda=6705.2$) to a difference in λ of 0.36 tenth-metre. The most refrangible of the components should also be the strongest.

The elements of the groups I. and III. (atomicity odd) have only doublets; triplets are found in the elements of group II. (atomicity even). As examples may be cited the doublets of Tl and the triplets of Hg.

Thallium.

λ_1 ...	5349.5	3528.3	3229.0	2921.3	2825.4	2710.4	2669.1	2609.4	2552.0	2517.0
ν ...	7792.6	7796.6	7794.9	7785.5	7766.1	7773.9	7783.1	7781.2	7794.2	7780.7
λ_2 ...	3775.6	2767.1	2579.7	2380.0	2317.0	2238.7	2210.0	2169.0	2128.6	2104.8

Mercury.

λ_1	5460.5	3662.9	3341.2	3021.0	2925.2	2798.5
ν_1	4633.0	4644.0	4638.0	4602.9	4644.7	4626.6
λ_2	4358.0	3130.4	2892.9	2652.2	2575.3	2477.7
ν_2	1763.4	1766.1	1776.4	1761.9	1759.0	
λ_3	4047.0	2966.4	2751.5	2533.8	2463.7	

With the triplets the ratio of the two constant differences $\frac{\nu_1}{\nu_2}$ increases from 2.01 in Mg to 2.63 in Hg. Also with these elements (of group II.) there are doublets, which follow the same rule as the others; the value of the difference ν_0 in these doublets is about 2.2 times as great as the first difference ν_1 of the triplets in the same element. For example, we have:—

	Ca.	Zn.	Cd.
ν_0	223.2	876.5	2483.8
ν_1	103.2	388.4	1172.5
$\frac{\nu_0}{\nu_1}$	2.16	2.23	2.12

These doublets contain the strongest lines of the elements of group II.

2. *The corresponding components of the doublets form series, of which the terms are functions of the consecutive integers. Each series is expressed approximately by an equation of the form*

$$n = n_0 - \frac{N_0}{(m + \mu)^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the wave-number, m any positive integer (the number of the term), $N_0 = 109721.6$, a constant common to all series and to all elements, n_0 and μ constants peculiar to the series. It will be seen that n_0 defines the limit which the wave-number n approaches to when m becomes infinite.

Messrs. Liveing and Dewar were the first to remark the existence of the series, as well as their different appearances. They are of three kinds: *diffuse*, *sharp*, and *principal* series. The first two are formed by the above-mentioned doublets or triplets; in the elements of the groups I. and III. there are consequently four different series of these two kinds, in the elements of group II. there are six. I have named them *first*, *second*, and *third* diffuse or sharp series. The lines of the first series of each kind are the strongest and the least refrangible.

Hitherto I have found the principal series only in group I. They are double, but the doublets are not of the same kind as those described in section 1; the components approach each other when m increases (see section 3). I name the stronger of the two series, which is also the most refrangible, *first principal series*. The principal series contain the strongest lines of the spectrum (in group I.), then come the diffuse series (the individual lines of which are in reality double; *c/r.* section 4), the sharp series are the weakest. In the individual groups the intensity decreases as the order of the series increases, in the same way as the lines grow weaker in the individual series with increasing m .

As an example of the series and their calculation, the principal series of *Li* is as follows:—

$$\text{Formula : } n = 43487 \cdot 7 - \frac{109721 \cdot 6}{(m + 0 \cdot 9596)^2}.$$

<i>m</i> ...	1.	2.	3.	4.	5.	6.	7.	8.	9.
λ obs.	6705·2	3232·0	2741·0	2561·5	2475·0	2425·5	2394·5	2373·5	2359·0
λ calc.	6704·8	3229·8	2740·5	2562·3	2475·3	2425·9	2394·9	2374·1	2359·5
Diff.	-0·4	-2·2	-0·5	+0·8	+0·3	+0·4	+0·4	+0·6	+0·5

3. The different series of the elements are related to each other in a way which proves that they all belong to one system of vibrations. To show these relations, I will cite as an example the formulæ of the diffuse and sharp lines of *Na*:—

Diffuse Group.

Sharp Group.

$$\begin{array}{l} \text{First series } n = 24481 \cdot 8 - \frac{109721 \cdot 6}{(m + 0 \cdot 9887)^2} \\ \text{Second series } n = 24496 \cdot 4 - \frac{109721 \cdot 6}{(m + 0 \cdot 9887)^2} \end{array} \quad \left| \quad \begin{array}{l} n = 24485 \cdot 9 - \frac{109721 \cdot 6}{(m + 0 \cdot 6445)^2} \\ n = 24500 \cdot 5 - \frac{109721 \cdot 6}{(m + 0 \cdot 6445)^2} \end{array} \right.$$

The series of the same group (diffuse or sharp) have the same value of μ ; the difference of their values of n_0 is equal to ν or (ν_1 and ν_2). This follows from the fundamental property of the doublets. With *Na* we have $\nu = 14 \cdot 6$.

The series of the same order (first, second, third) have the same value of n_0 in the different groups; they are distinguished by the values of μ . The difference, for instance, of the numbers 24481·8 and 24485·9, which are perfectly independent of each other, amounts only to 0·7 tenth-metre. We find in all the revised spectra the same accordance when we calculate the values of n_0 , using only the last terms of the series. For example, if we denote the values obtained from the diffuse series by n_1 and those from the sharp series by n_2 :—

Element ...	Li.	Mg.	Cd.	Tl.
n_1	28598·5	39777·9	40775·9	41485·9
n_2	28601·1	39779·9	40789·1	41486·5

Between the principal and the sharp series there is also a very close relation. For if we write the equation (1) in the more symmetrical form

$$\pm \frac{n}{N_0} = \frac{1}{(m_1 + \mu_1)^2} - \frac{1}{(m_2 + \mu_2)^2}, \quad . \quad . \quad . \quad (2)$$

it is found that this equation, without varying the constants μ_1 and μ_2 , will represent a principal series or a sharp series, according as we assume the one or the other of the integers m_1 and m_2 to be variable; to the number which is left unchanged we must assign the value 1.

To calculate with great approximation the spectrum of one of the alkaline metals, we use only four constants (with Li but three), the common constant N_0 not included.

By the proposal of a *system of notation* for series and lines, I have tried to show a way by which we can indicate shortly the connexion of the different parts of a spectrum with the whole system of vibrations, and which at the same time allows the correspondence of the lines of different elements clearly to appear. A few examples will suffice to show the arrangement and the use of this system. K [D₁, 4] denotes the fourth line of the first diffuse series of the spectrum of potassium ($\lambda=5801$); Mg [S₂] the (whole) second sharp series of Mg ($\lambda=5172\cdot0, 3331\cdot8, 2938\cdot5, 2778\cdot7, 2695, 2646$); Rb [P₁₂, 2] the second doublet of the principal group of Rb ($\lambda=4202$ and 4216); the single lines are denoted by Rb [P₁, 2] and Rb [P₂, 2] respectively.

4. *The wave-lengths (and the wave-numbers) of corresponding lines, as well as the values of the constants ν , n_0 , μ of corresponding series of different elements, are periodical functions of the atomic weight.*

As an example, the wave-lengths of the second term ($m=2$) of the diffuse series may be taken together with the values of ν (with the triplets ν_1 and ν_2), which are given in smaller figures in their respective places between the wave-lengths. These values of ν are means from the differences of the wave-numbers of all doublets which have been employed in the calculation. The components of the doublets are themselves double; the less refrangible of the secondary components is the weaker, but corresponds to the constant difference, and is consequently to be reckoned as the true component of the doublet.

Group of elements.		Li.	Na.	K.	Cu.	Ag.	Au.
I.	λ_1	{ 6102 14·8 (0·8 calc.)	8199	{ 5217·1 242·2 5152·6	{ 5470·0 5460·0	{ 5862·0 5836·0
	ν		14·8	56·4		917·2	3819·5
	λ_2		8187		5208·7	4792·0
		Be.	Mg.	Ca.	Zn.	Cd.	Hg.
II.	λ_1	{ 3130·3 3130·0	3837·9	{ 4455·2 4454·0	{ 3344·4 388·4 3301·7 187·4 3281·7	{ 3611·8 3609·4	{ 3662·9 3654·4
	ν_1		41·4	103·2		1160·2	4637·3
	λ_2		3832·1	{ 4435·3 4434·5		{ 3466·7 3465·2	{ 3130·4 3124·5
	ν_2		20·6	51·4		538·4	1766·0
	λ_3		3829·2	4425·0		3402·7	2966·4
		B.	Al.			In.	Tl.
III.	λ_1	{ 2497·0 10·5 2496·2	3091·9	{	{ 3257·8 3255·5	{ 3528·3 3517·8
	ν		109·6		2212·4	7784·2
	λ_2		3081·2		3038·7	2767·1

The lines of Li and K are, in all probability, double like the others, but their components have not yet been separated.

The periodical variation of the constants allows of calculating by interpolation the spectrum of an element when the spectra of the adjacent elements in the periodical system are known. To show how far such an interpolation can go, I will cite the wave-lengths of the first terms of the diffuse and sharp series of Ga. They are calculated without making use in any way of the (two) measured lines of this element, or even having them present in the calculation.

The interpolated constants are (*cfr.* section 3):—

First series	n_0 47547·1	ν 831·6	Diffuse group	μ 0·8363
Second series	48378·7		Sharp group	0·1568

and the thereby calculated wave-lengths:—

m	Diffuse group.			Sharp group.		
	1.	2.	3.	2.	3.	4.
First series ...	6663·4	2949·2	2494·3	4173·7	2737·0	2427·4
Second series...	6313·5	2878·6	2443·6	4033·7	2676·1	2379·3

The sharp doublet ($m=2$) is nearly coincident with the two lines which hitherto have been measured. The wave-lengths of these lines are, viz :—

After Lecoq de Boisbaudran.	After Deville and Mermet.
$\left. \begin{array}{l} 4170 \\ 4031 \end{array} \right\} \nu = 826.9$	$\left \begin{array}{l} 4171 \\ 4033 \end{array} \right\} \nu = 820.3$

The accordance is even better than could well be expected.

Finally, I will remark that the hypotheses of Mr. Lockyer on dissociation of the elements are quite incompatible with the results of my researches. The observations of Lockyer within the spectra of Na and K prove only that, with luminous atoms as with sounding bodies, the relative intensity of the partial tones may vary under different circumstances. For the lines in question belong, without doubt, to the same system of vibrations.

Lund, February 1890.

XXXV. *The Change of the Order of Absolute Viscosity encountered on passing from Fluid to Solid.* By CARL BARUS.

1. **T**O my knowledge nobody has thus far defined the difference between the solid state and the fluid states quantitatively. In the case of liquids and gases viscosity can be absolutely expressed with facility, and the data have therefore to be stated with considerable rigour. This is not true for solids, where the results are relative throughout.

The present paper submits two methods for the coordination of the viscous behaviour of solids and of liquids. In describing the differential method applied by Dr. Strouhal and myself†, we incidentally pointed out the way in which the relative viscosity of two solids may be stated in terms of the respective sectional areas, by which the motion at the junction of the two counter-twisted wires or rods is annulled. Suppose that one of the wires is a solid, whereas the other is a very viscous liquid. Then if the viscosity of the latter can just be measured by transpiration-methods (§§ 4, 5), it follows that the viscosity of the true solid with which it was counter-twisted may also be absolutely expressed. This indicates the first method of the present paper (§§ 8, 9).

* Communicated by the Author.

† Barus and Strouhal, *American Journal*, xxxiii, p. 29 (1887).

My second method for measuring the viscosity of solids absolutely is direct. It is capable of yielding results of any desirable accuracy, supposing the necessary facilities for an adjustment free from vibratory disturbances are given (§§ 12, 13).

Gases and Vapours.

2. Results for the viscosity of gases and vapours are given by many observers*. The data present some curious aspects; thus, for instance, the viscosity of vapours† is frequently smaller than the viscosity of gases. The order of viscosity (η) is about $10^{-4}g/cs$ (cf. § 18.). Results for the viscosity of substances in the neighbourhood of Andrews's critical temperature are not available. Such an investigation would be highly desirable (§ 18).

Liquids.

3. The literature contains extensive researches and is systematized in Landolt and Boernstein's Physical Tables‡. The data are easily expressed absolutely, by aid of Slotte's§ values of the viscosity of water between 0° and 100° . If water at 20° be taken as a type liquid, $\eta = \cdot 01 (g/cs)$ (cf. § 18).

Viscous Liquids.

4. Data are wanting.

My experiments were made with marine glue||. The method is simple. A fairly wide capillary tube, abc , provided with a cylindrical open reservoir, a , at one end, was half filled with marine glue, the thread extending from the reservoir, a , as far down as the middle, b , of the tube. The other (open) end of the tube was inserted into the flask, $dddd$, from which the air was then exhausted. Thus a pressure of about 1 atm. is continually brought to bear on the reservoir a of the tube, the other end, c , being *in vacuo*. A lateral arm, e , closed by fusion, facilitates the exhaustion. A small vacuum-

* Summarized in O. E. Meyer's *Die kinetische Theorie der Gase*, Breslau, 1877, pp. 138 *et seq.*

† The most complete set of data are those of Puluĵ, Phil. Mag. [5] vi. p. 157 (1878). Lothar Meyer, E. Wiedemann, and others have contributed to the subject.

‡ *Physikalisch-chemische Tabellen*: Berlin, J. Springer, 1883, p. 153.

§ Slotte, Wied. Ann. xx. p. 267 (1888). References to other researches (O. E. Meyer, Poiseuille, Rosencranz) are there given.

|| A valuable cement being (nominally) a specially prepared mixture of rubber and shellac. It has a pitchy consistency, and can be thickened by adding shellac.

gauge, *g g*, held in place by a layer of paraffin, *h*, shows the observer to what degree the vacuum is maintained in the lapse of time. A number of tubes, *abc*, may be inserted side by side, and it is always necessary to coat the stopper with cement.

5. The transpiration-equation due to Poiseuille, theoretically corrected by Hagenbach*, has the form

$$\eta = \frac{\pi P r^4}{8 v l} t - \frac{m}{2^{10/3} \pi l} \frac{1}{t}, \quad (1)$$

where η is the absolute viscosity of the liquid, v the volume, and m the mass transpiring through the capillary length l and radius r , in the time t . In the present case of excessively slow transpiration the correction may be neglected. P is the pressure-excess, in dynes per square centimetre. All magnitudes are to be expressed in C.G.S. units.

In the above form of apparatus (fig. 1) l is not constant, and v is measured in terms of the increase of length of the capillary thread *ab* (fig. 1). Hence the differential equation corresponding to (1), since $dv = \pi r^2 dl$, is

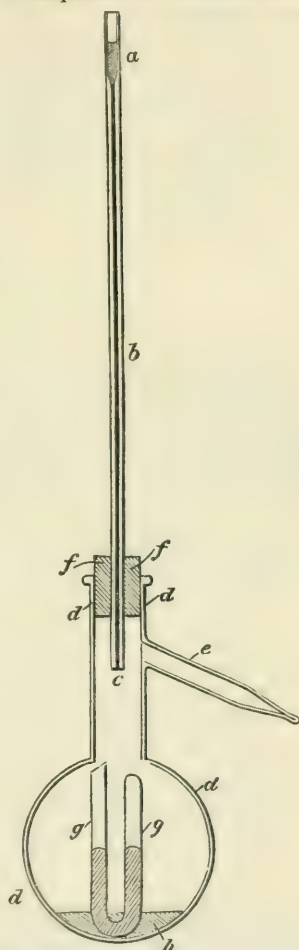
$$\eta = \frac{P r^2}{8 l} \frac{dt}{dl} \quad \dots \dots \dots (2)$$

Integrating between 0 and t , and between l_1 and l_2 ,

$$\eta = P r^2 t / 4 (l_2^2 - l_1^2). \quad \dots \dots \dots (3)$$

Here l_1 is the original length ($t=0$), and l_2 the final length

Fig. 1.—Apparatus for the Secular Transpiration of Viscous Liquids.



* Pogg. *Ann.* cix. p. 358 (1860). This reference is incidental, or I should have to refer to Poisson, Navier, Stokes, Stefan, Helmholtz, and others.

of the thread of marine glue. The effect of the cylinder of viscous fluid in the reservoir *a* may be neglected from its large radius.

5*a*. By way of digression I may add another similar case; viz. that of a viscous liquid like glycerine, transpiring in a vertical capillary tube, in virtue of the weight of its own column only. In this case $P = (L + l)\delta g$, δ being the density of the liquid, g the acceleration of gravity, L the initial head of the column. Inserting these quantities and integrating, equation (2) becomes

$$\eta = \frac{\delta g r^2}{8 \left(l_2 - l_1 + L \ln \frac{L + l_1}{L + l_2} \right)} t.$$

An example of results obtained in this way is given in the following Table. The observations, though made upon a single descending thread at the end of each half minute, are grouped in two batches. The tube was dry; perhaps a moist tube (adhering thin film of glycerine) would have been preferable.

EXAMPLE.—Viscosity of Glycerine.

$r = .0505$ centim.; $L = 1.35$ centim.; $\delta = 1.26$; $\Delta t = 120$ sec.

<i>t.</i>	<i>l.</i>	η .	<i>t.</i>	<i>l.</i>	η .
sec.	cm.	<i>g./cs.</i>	sec.	cm.	<i>g./cs.</i>
30	10.07	5.05	270	20.82	5.53
150	20.30		390	38.60	
60	12.72		300	31.95	
180	22.75	5.07	420	40.83	5.46
90	15.30		330	34.20	
210	25.10		450	43.04	
120	17.80	5.13	360	36.40	5.43
240	27.43		480	45.22	

To account for the difference of η in the two sets of results is beyond the present purpose. It is noteworthy* that each measurement of η occupies but two minutes, even admitting that the tube is unfavourably wide; for in the case of viscous liquids the temperature-effect is of great importance, and this expeditious method therefore has some advantages. The experiment may be varied by observing the descending upper

* Cf. Graham, *Phil. Trans.* cli. p. 382 (1861):—"The liquid (glycerine) is too viscous to be transpired by means of the bulb and capillary employed in these experiments." I am not aware that the viscosity has been measured since.

meniscus, while the lower end of the capillary is submerged in glycerine.

6. By applying equation (3) I obtained the η expressed in the following Table:—

TABLE I.—Transpiration of Marine Glue.

$P = 10^6$ dynes ; $r = .0406$ centim. ; temperature (say) = 25° .

Date.	t .	l .	$\eta \times 10^{-6}$.
	sec.	cm.	c/gs.
May 7, 1889. 12 ^h	0	3.7	
Dec. 7, 1889, 12 ^h	18.5×10^6	7.2	200

This is a striking result, remembering that a sphere of the cement, if placed on a plane surface, will run out to a flat cake in a few months. Nevertheless this type of viscous fluid is 20 billion times as viscous as water at the same temperature.

After long continued transpiration the thread of marine glue shows two strata. The advance portion is amber-coloured and less viscous, the rear portion brown, clearly containing most of the shellac. Hence the observed η is probably somewhat low. (*Cf.* § 10.)

7. Paraffine (melting-point 55°) treated in the same way showed no transpiration. The tube ($2\rho = .082$ centim.) was nearly of the same bore as above, and the length of thread in the most favourable case 2.2 centim. The motion, if any, must have been below .01 centim. Hence the viscosity of the paraffine must be greater than 2×10^{11} g/cs at about 25° . It is nearly impossible to insert a capillary paraffine thread in a tube, free from the vacuum-bubbles due to contraction on cooling.

Solids.

8. Having obtained the result in § 6, I proceeded to use it for obtaining the viscosity of hard steel by the method of comparison indicated in § 1. The apparatus was essentially like that of my earlier experiments*. To secure additional safety† I introduced the principle of substitution, whereby the steel wire and the rod of marine glue were consecutively subjected to known torsion-couples, in ways otherwise identical. From the enormous viscosity of steel, as compared

* From the context it appears that the method of substitution is probably necessary.

† American Journal, xxxiv. p. 2 (1887).

even with marine glue, a beam of this substance, say a decimetre thick, would show about the same deformation initially as a steel wire only a millimetre thick, *cæt. par.* So large a mass of the cement is inconvenient to handle. I therefore used a rod about 4 centim. thick and suitably apportioned the torsion-couples in the two cases. The results are given in Tables II. and III., where 2ρ is the diameter, l the length, of the similarly twisted rods. This twist τ is given in the first column, and is proportional to the applied couples. N denotes the viscous motion at the index, at the time specified, and is given in scale-parts (distance between mirror and scale 200 centim.). Reduction of N is not necessary, since the present purposes are comparative. The steel wire is twisted alternately in opposite directions to allow for the accommodation. In Table II. this precaution is superfluous, the substance being a fluid. The three sets of data are merely given to show the behaviour more fully. Other experiments made with the cement may be omitted here.

TABLE II.—Viscous Deformation of Hard Steel. Wire No. 1.
 $\rho = 0.40$ centim. ; $l = 30$ centim.

τ .	Time.	$N \times 10^2$.	τ .	Time.	$N \times 10^2$.	τ .	Time.	$N \times 10^2$.
	minutes.	cm.		minutes.	cm.		minutes.	cm.
+5.7	0	Twisted.	-5.7	0	Twisted.	+5.8	0	Twisted.
	2	0		2	- 0		2	0
	3	70		3	- 71		4	40
	4	115		4	-125		3	72
	6	187		6	-200		6	122
	8	235		8	-258		8	160
	10	278		10	-301		10	190
	12	315		12	-340		12	212

TABLE III.—Viscous Deformation of Marine Glue.
 $\rho = 2$ centim. ; $l = 30$ centim.

τ .	Time.	$N \times 10^2$.	τ .	Time.	$N \times 10^2$.	τ .	Time.	$N \times 10^2$.
	minutes.	cm.		minutes.	cm.		minutes.	cm.
*1.4	0	0	1.4	0	0	1.4	0	0
	2	260		2	250		2	220
	3	480		3	450		3	420
	4	710		4	700		4	610
	5	910		5	900		5	810
							6	1010

* This refers to the applied couple. The initial twist of the bar of marine glue is practically zero.

9. From these Tables the mean rate of motion of marine glue appears as 2 centim. per minute, whereas the corresponding mean motion for hard steel is (say*) .4 centim. per minute, for the three cases. The couple acting on the cement is $1.4x$, while the couple in the other case is $5.7x$. Since the cement is a fluid, the rate of motion for identical couples would be 8 centim.

The principle given in § 1 may now be applied, whereby viscosities are inversely as the fourth power of the radii, *cæt. par.* Let η' and η be the viscosities of marine glue and hard steel respectively. Then

$$\eta = \eta' \left(\frac{2.00}{.04} \right)^4 \frac{8.0}{.4} = \eta' \times 10^9 / 8. \quad . \quad . \quad . \quad (1)$$

From Table I., $\eta' = 200 \times 10^6$; hence the mean viscosity of originally untwisted glass-hard steel, during three consecutive alternate twists of 12 minutes each, just within the limits of rupture is at least

$$\eta = 25 \times 10^{15} \text{ g/sc.} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

10. The present results subserve their chief purpose in furnishing an estimate of the order of viscosity of glass-hard steel; for the unavoidable errors encountered in a comparative method like the present are not insignificant. In the first place the thread of marine glue observed for transpiration in § 6 during half a year is not identical with the rod of this material which is twisted (§ 8), neither as to temperature nor composition (*cf.* remarks end of § 6). Possibly better results might be obtained with old pitch. Again, the rod of marine glue, while it is being twisted, is also being appreciably stretched by its own weight. This complicates the angular measurement. Finally, the sectional error of an opaque rod, not necessarily free from air-bubbles, is considerable. Equation (3) must therefore be looked on as assigning an order to the viscosity of hard steel above 10^{16} g/cs.

11. Before giving the results of the following direct method, it is expedient to insert a paragraph on the viscosity of solids generally. In § 8, while the steel wire is strained by the couple almost as far as the limits of elasticity permit, the rod of marine glue is initially scarcely strained at all. In the latter case, however, the unstable configurations essential to viscous motion are supplied in relatively great numbers by the ever changing distribution of the heat-agitation within the body. In a homogeneous solid free from strain (soft steel)

* The viscosity of solids being a function of time, strain, and temperature. This distinction is beyond the purposes of the above paragraph, but will be fully carried out below, in §§ 11 *et seq.*

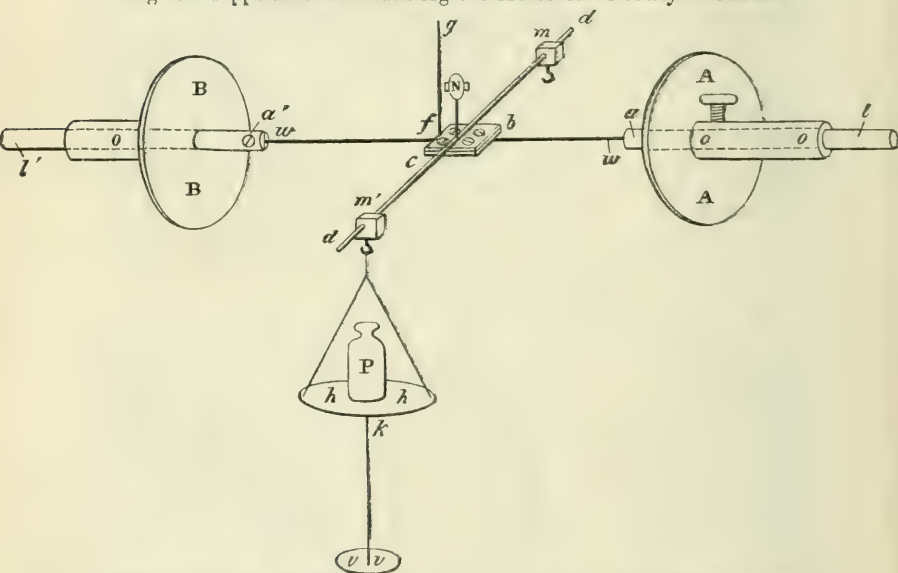
such configurations practically vanish as to number. I doubt whether in soft steel the viscous deformation due to instantaneous exceptionally intense molecular motion at different points within the solid, could be recognized at ordinary temperatures. The case is different when the solid is under stress. Any twist, no matter how small (?), is accompanied by a proportionate amount of permanent strain, with which a corresponding amount of instability is necessarily associated. Hence it must be borne in mind that the viscosities expressed absolutely below refer to steel in a condition of strain just within the elastic limits.

I can here merely allude to the very recent and suggestive paper of C. H. Carus-Wilson (*Nature*, xli. p. 213, 1890), in which the behaviour of steel near the elastic limits is interpreted in analogy with the well-known circumflexed isothermals of condensable gases, due to James Thomson.

Now it is clear that if stressed steel be left to itself, the number of unstable configurations becomes rapidly less as the time after twisting increases. Energy is dissipated. The viscosity of solids is therefore essentially a time-function as well as a strain-function.

12. The apparatus with which the following absolute results

Fig. 2. — Apparatus for measuring the Absolute Viscosity of Solids.



were obtained is shown in fig. 2. AA and BB are two massive torsion-circles, the hollow cylindrical shafts, *o o*, of

which are firmly clamped to supports projecting from the wall of the room. The steel wire, ww , to be tested is tensely drawn between the cylindrical cores, al , $a'l'$, and clamped without torsion. To accomplish this the ends of the wire are bent hook-shaped, and inserted in flat fissures at the ends of the rods al , $a'l'$, the clamp-screw (shown at a') passing through the hooks of the wire. The middle part of ww carries a pair of plates, bc , held together by four screws in such a way as to clamp the wire firmly between the plates. A brass rod of screw-wire, dd , is soldered to the upper plate, and when in adjustment is horizontal and at right angles to the axis of ww . Thus the rod dd is virtually the beam of a balance, and two small nuts, mm' , symmetrically placed near the ends of dd , are provided with hooks from which a scale-pan, hh , may be suspended. The latter carries a light horizontal disk, ee , to be submerged in water (not shown), with the object of deadening vibrations when the apparatus is in adjustment. The upper plate bc also carries an adjustable mirror, N , for angular measurement, as well as an index, fg , moving across a stationary graduated dial (not shown) by which the amount of twist holding the weight, P , in equilibrium is roughly registered.

In adjusting the apparatus, the scale-pan hh is removed and the rods al so placed that the lever dd is vertical. After clamping al (care being taken to avoid twisting ww) the scale-pan is attached at m' , and additional weights P added to hold the lever dd horizontal. Hence the two halves of the wire ww are twisted 90° each for the whole length. Other twists may be applied by rotating the torsion-circles together (it would be necessary to connect them rigidly for this purpose) and adding suitable weights P .

To fasten the wire securely between the plates the lower one is clamped horizontally in a vice. If there were rotational sliding possible here it would be detected in examining very viscous wires. Some difficulty is experienced in fixing ww in place quite free from initial torsion. There is also some flexure; but for wires of the radius given these discrepancies may be disregarded. When AA and BB are rigidly connected, the twist of the wire ww may be expressed in terms of the load P .

13. To complete the results obtained with this apparatus, let 2ϕ be the amount of angular viscous motion*, in radians, of any right section of the wire relative to another right section, whose distance from the first is the unit of length. Suppose, furthermore, that in the plane of a right section

* The factor 2 is supplied conformably with my earlier notation.

there is no shearing. Then $2d\phi/dt=2C_t$ is the common angular velocity, per unit of length, with which the shear is increased. Consider an elementary cylindrical shell whose length l is the effective length of either half of the wire ww (fig. 2), and whose right section is $2\pi r dr$. Then the amount of force distributed uniformly over $2\pi r dr$ will be

$$df=\eta_t \frac{2\pi r dr}{l} (l2C_t r). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Multiplying by r , and integrating between 0 and ρ , the radius of the steel wire,

$$\frac{1}{2} P\lambda = \eta_t \frac{\pi \rho^4}{2} 2C_t, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $P/2$ is the weight at the end of the lever-arm λ , per effective half of the wire. In any given adjustment $P\lambda/\pi\rho^4=A$ = constant. Hence

$$\eta_t = A/2C_t. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In these equations it has been assumed that $\int \eta r^3 dr = \eta_t \int r^3 dr$. Hence under all circumstances η_t is a mean value defined by these integrals.

14. Results obtained with the apparatus § 12, are given in Tables IV. to VII. Here ρ is the radius, l the length of each effective half of the steel wire. P is the total force (being the weight plus the weight of the scale-pan) acting at the end of the lever λ (see fig. 2). The rate of twist is given under τ , and 2Φ is the total yield during the interval of experiment. N denotes the actual scale-reading observed by the telescope (scale-distance from mirror, $R=200$ centim.) at the time given; and 2ϕ is the viscous angular motion between two right sections of the steel wire 1 centim. apart.

In the second half of the tables, $2C_t$ is the time-rate of change of 2ϕ , computed for consecutive intervals of 500 seconds each. The final column contains the corresponding absolute viscosity. All times are reckoned from the moment of twisting. To obtain $2C_t$ I availed myself of graphic methods*, these being in conformity with the mean accuracy of the work. Table IV. contains results for the wire No. 1, already tested in Table I. Three twists are applied, alternately in opposite directions. In Table V. the same wire is similarly examined, after it has been softened by heating to

* Of course a set of smoother values might be obtained by computing the constants of the curves ϕ from Kohlrausch's exponential formula, and the tangents from the values obtained.

redness and cooling in air. Table VI. contains data for a new glass-hard steel wire, originally free from stored twist. Table VII., finally, contains the viscous behaviour of a wire tempered at 450° , which was used as a normal in my former differential experiments.

TABLE IV.—Absolute Viscosity of a Glass-hard Steel Wire.
No. 1. Fourth Twist.

$l=12.9$ centim. ; $\rho=.0405$ centim. ; $P=82 \times 981$ dynes ;
 $\lambda=9.43$ centim.

$\frac{\tau}{2\phi}$.	Time.	$N \times 10^2$.	$2\phi \times 10^6$.	Time.	$2C_t \times 10^9$.	$\eta_t \times 10^{-15}$.
Radians.	Sec.	Centim.	Radians per centim.	Sec.	Radians per centim. per sec.	$g/cs.$
$\cdot 12$	0	Twisted.		0		
	420	0	*0	500	735	122
	720	104	202	1000	462	194
	1020	180	349	1500	310	291
	1860	320	621	2000	222	405
	2220	360	698	2500	183	491
	2820	417	808	3000	150	600
	3480	465	901			

No. 1. Glass-hard. Fifth Twist.

$\cdot 12$	0	Twisted.		0		
$\cdot 009$	480	*0	*0	500	*910	99
	840	120	233	1000	474	190
	1320	235	456	1500	347	259
	1860	329	638	2000	270	333
	2400	402	779	2500	230	391
	2940	464	900	3000	210	428
	3480	520	1008			

No. 1. Glass-hard. Sixth Twist.

$\cdot 12$	0	Twisted.		0		
$\cdot 009$	360	0	0	500	467	193
	960	120	233	1000	265	339
	1260	160	310	1500	193	466
	1800	210	407	2000	156	577
	2340	250	485	2500	138	652
	3120	306	593	3000	126	715
	3900	353	684			

* The minus signs, being without interest in this and the following similar series, are omitted for brevity.

TABLE V.—Absolute Viscosity of Soft Steel, being Wire No. 1, heated to redness and cooled in air. First Twist.

$l=13\cdot0$ centim.; $\rho=.0405$ centim.; $P=82\times981$ dynes;
 $\lambda=9\cdot43$ centim.

$\frac{\tau}{2\phi}$.	Time.	$N\times10^2$.	$2\phi\times10^6$.	Time.	$2C_t\times10^9$.	$\eta\times10^{-15}$.
Radians.	Sec.	Centim.	Radians per centim.	Sec.	Radians per centim. per sec.	$g/cs.$
$\cdot12$	0	Twisted.	0	0		
$-\cdot007$	420	0	0	500	220	409
	900	40	77	1000	89	1010
	1500	63	121	1500	63	1430
	2100	80	154	2000	47	1920
	2700	92	177	2500	34	2650
	3380	98	188	3000	26	3460
	3780	103	198			

No. 1. Softened. Second Twist.

$\cdot12$	0	Twisted.	0			
$\cdot010$	360	0	0	500	164	550
	1020	50	96	1000	116	776
	1500	70	135	1500	59	1520
	1983	82	158	2000	40	2250
	2520	93	179	2500	30	3000
	3120	100	192	3000	15	6000

No. 1. Softened. Third Twist.

$\cdot12$	0	Twisted.	0			
$-\cdot007$	240	0	0	200	138	652
	840	42	81	1000	70	1290
	1560	64	123	1500	40	2250
	2100	74	142	2000	28	3210
	2520	76	146	2500	17	5300
	2640	78	150	3000	14	6400
	3120	81	156			

TABLE VI.—Absolute Viscosity of Glass-hard Steel. Wire No. 2. First Twist.

$l=13.0$ centim.; $\rho=.0405$ centim.; $P=82 \times 981$ dynes;
 $\lambda=9.43$ centim.

$\frac{\tau}{2\phi}$	Time.	$N \times 10^2$	$2\phi \times 10^3$	Time.	$2C_t \times 10^3$	$\eta_t \times 10^{-1}$
Radians.	Sec.	Centim.	Radians per centim.	Sec.	Radians per centim. per sec.	$g/cs.$
.13	0	Twisted.	0	0		
— .009	120	0	0	500	660	136
	420	186	358	1000	325	277
	720	270	520	1500	230	391
	1080	335	644	2000	180	500
	1620	410	789	2500	140	643
	2100	458	881			
	2580	495	952			
	3000	518	996			

No. 2. Glass-hard. Second Twist.

— .13	0	Twisted.	0	0		
.010	240	0	0	500	683	131
	600	144	277	1000	392	229
	900	220	423	1500	285	316
	1260	288	554	2000	240	375
	1800	365	702	2500	205	439
	2100	404	777			
	2460	450	865			
	2700	470	904			
	3000	502	965			

No. 2. Glass-hard. Third Twist.

	0	Twisted.	0			
	240	0	0			
	600	117	225			

Wire breaks spontaneously.

TABLE VII.—Absolute Viscosity of Steel, annealed at 450°. Wire No. 15. Twisted indefinitely.

$l=13.6$ centim.; $\rho=.0405$ centim.; $P=82 \times 981$ dynes;
 $\lambda=9.43$ centim.

$\frac{\tau}{2\Phi}$	Time.	$N \times 10^2$	$2\phi \times 10^6$	Time.	$2C_t \times 10^9$	$\eta_t \times 10^{-15}$
Radians.	Sec.	Centim.	Radians per centim.	Sec.	Radians per centim. per sec.	$g/cs.$
.12	0	Twisted.	0	0		
-.002	240	0	0	500	177	508
	720	51	94	1000	69	1300
	1200	71	131	1500	40	2250
	1860	86	158	2000	32	2810
	2520	95	175	2500	25	3600
	2000	101	186	3000	20	4500
No. 15. Tempered at 450°. Next Twist.						
-.12	0	Twisted.		0		
.003	240	0	0	500	111	811
	600	26	48	1000	46	1950
	1200	43	80	1500	40	2250
	1740	54	100	2000	34	2650
	2580	68	125	2500	31	2910
	3240	81	149	3000	30	3000
No. 15. Tempered at 450°. Next Twist.						
.12	0	Twisted.		0		
-.003	240	0	0	500	180	500
	660	48	88	1000	82	1100
	1260	78	143	1500	57	1570
	1740	92	169	2000	48	1870
	2520	112	206	2500	45	2000
	3120	126	232	3000	42	2140

Some irregularities are apparent, largely introduced by vibrations against which our laboratory facilities afford no adequate protection. Vibrations increase the rate of twist

periodically, and thus supply a greater number of instabilities than correspond to the mean twist (position of equilibrium) in question. They may also have a more direct molecular effect in decreasing viscosity. When the rate of twist in the two wires is unequal, viscous motion will also be in excess of the true value. This also applies in case of slightly different lengths, l , of the two effective halves of the wire. In the case of No. 15, which had become somewhat worn by use, the load P probably strained the wire too near the elastic limits. This I infer from the observed successive reduction of viscosities from twist to twist, clearly indicating that an excess of instability is being supplied. It is therefore better to accept the behaviour of No. 2 (soft) as typical of No. 15; for the normal viscosities of the two states of temper are identical.

Discussion.

15. Turning first to the values of ϕ , it is seen at once that they substantiate the inferences of my earlier papers throughout*. They therefore need no further comment here. Tables V., VII. contain data for my normal wire, by aid of which the differential results of the earlier papers may be reduced to absolute values. I have endeavoured to make the angles τ of nearly the same value in all cases, so that ϕ/τ may be comparable.

16. The spontaneous breaking of the glass-hard wire in Table VI. deserves mention. It occurred during the third twist, and at a time when the wire was in no way interfered with. This corresponds to the spontaneous explosion of hard projectiles frequently observed. It also corresponds to the spontaneous rupture of stressed glass, whether the stress be stored internally or applied externally. I have observed this interesting phenomenon in glass under a great variety of

* Phil. Mag. xxvi. p. 183 (1888); *ibid.* xxvii. p. 155 (1889).

In the deductions of the former paper (p. 189) I neglected the elastic motion, in virtue of which, at every stage of viscous yielding, the rate of twist is maintained constant throughout the system. After correcting for this,

$$L\psi = 2l' \{ \phi_3(\beta - l') + \phi(\alpha - \beta) + \phi_1(L - \alpha) \} - 2l\phi'l';$$

which under the simplified conditions of experiment becomes $\psi = l(\phi - \phi')$. Hence it follows that the data $(\phi - \phi')$ of the two papers cited are relative, and must be multiplied by $\ln 2$ to reduce them to the dimensions defined in the text. Beyond this the error is without importance, the data applying at once to reeds initially somewhat harder than those actually observed.

conditions. In all cases there is gradual molecular change, and the solid finally breaks without any apparent cause.

17. The chief results of Tables IV. to VII. are the values η_t , whether they be regarded as time-functions, or as exponents of the *solidity* of steel. In fig. 3 these data are constructed graphically. An inspection of the figure shows at once that both solid viscosity and its rate of increase with time are magnitudes which increase together (Tables IV., VI. compared with Tables V., VII.). After about an hour has elapsed since twisting, the viscosity of hard steel may be quite as large as the initial viscosity of soft steel; but at corresponding times the viscosity of soft steel continues to be more and more pronouncedly the greater.

The curves are not consistent as to curvature. This may be best inferred from the hard wires, where the viscosities are smaller, the deformations large, and the observations therefore as a whole much more accurate (Tables IV., VI.). Hence I regard the promiscuous irregularities of fig. 3 as due to errors of observation and construction. According to the law of F. Kohlrausch*, $-d\phi/dt = a\phi/t_n$, where a and n are constants. In case of small torsions or short times, $-d\phi/dt = a\phi/t$ suffices. Thus for the purpose of deducing the time-rates, κ , of increase of solid viscosity, it is permissible to regard the curves of fig. 3 as essentially linear.

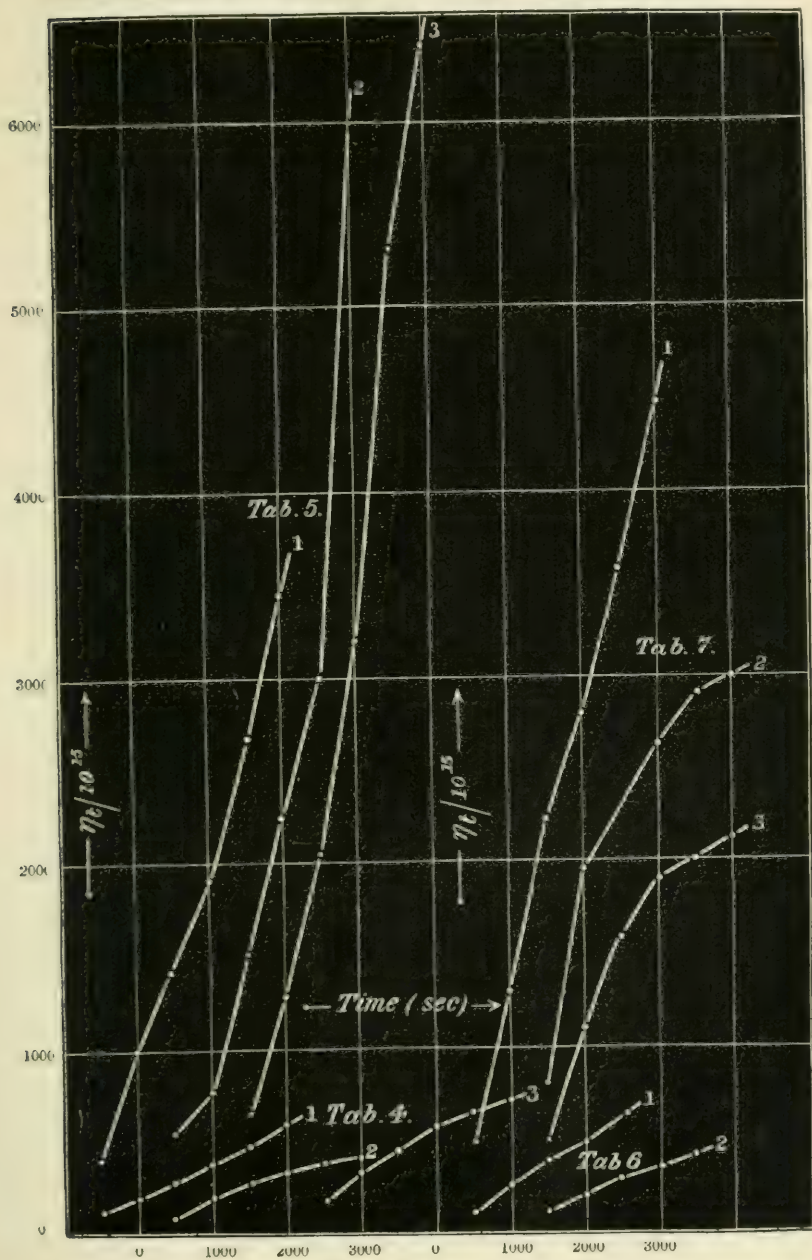
This is done in the following table.

TABLE VIII.—Mean time-rate of increase of the absolute Viscosity of Steel, hard and soft.

Hard Steel.			Soft Steel.		
	Twist No.	$\kappa \times 10^{-12}$.		Twist No.	$\kappa \times 10^{-12}$.
		g/cs^2 .			g/cs^2 .
Table IV...	4	220	Table V...	1	1200
	-5	140		-2	1400
	6	240		3	1900
Table VI...	1	230	Table VII.	1	1500
	-2	140		-2	1200
				3	1000
Mean rate κ		194×10^{12}	Mean rate κ		1400×10^{12}
Mean viscosity at 500 sec.		140×10^{15}	Mean viscosity at 500 sec.		570×10^{15}

* Kohlrausch, Pogg. Ann. cxxviii. p. 216 (1866).

Fig. 3.—The Absolute Viscosity of Hard Steel (Tables IV., VI.) and of Soft Steel (Tables V., VII.), considered in its variation with the time elapsing after twisting.



The general explanation of these results has been indicated in § 11. In a liquid or a viscous fluid under moderate stress the instabilities are supplied by the mere thermal agitation at ordinary temperatures, at the same rate in which they are used in promoting viscous motion. Hence viscosity is constant at a given temperature. In a solid under stress the instabilities are expended at a rate decidedly greater than the small rate of continuous supply. Thus viscosity decidedly increases with time. Suppose, therefore, a solid of initially greater viscosity starts on its viscous deformation at an instant when the viscosity of a solid of initially smaller viscosity has been increased by time to the initial value of the former case. This can actually be realized by twisting a soft steel rod about an hour later than a hard steel rod (fig. 3). Then, in succeeding times, even though the substances start at a state where both are equally viscous, the viscosity of the initially more solid body will rapidly overtake the other; for the supply of instability due to temperature alone is continuously greater in one case than in the other.

18. Summarizing the results of the above paragraphs, the viscosities of the three states of aggregation may be expressed in terms of the absolute *g/cs* scale as follows:—

TABLE IX.—Viscosity, considered in its Variations with the State of Aggregation.

Gases and Vapours.		Andrews's critical state.		‡ Liquids.	
Substance.	η .	Substance.	η .	Substance.	η .
* Ether, 0°	6.8×10^{-5}	?	?	Ether, 30° ...	9×10^{-4}
* H ₂ , 0	8.7×10^{-5}			Ether, 10 ...	1.9×10^{-3}
* Air, 0	1.75×10^{-4}			Water, 97 ...	3.0×10^{-3}
† O ₂ , 0	2.12×10^{-4}			Water, 20 ...	1.0×10^{-2}
				§ Glycerine ...	5
Range	10^{-5} to ?	?	to ?	Range	? to 10^{-2}

* Puluj, *l. c.*

† O. E. Meyer, *l. c.* p. 142.

‡ Landolt and Boernstein's Tables, *l. c.*, and Slotte, *l. c.*

§ A rough measurement of my own, § 5a. Graham's results, 'Phil. Trans.' 1861, p. 373, refer to dilute glycerine.

Table IX. (continued).

Viscous Fluids.		Solids.	
Substance.	η .	Substance.	η .
Marine glue	2×10^9	Paraffine at 20° (m.p. 55°). }	$> 2 \times 10^{11}$
		† Hard steel, glass &c. }	$\begin{cases} 10^{17} \text{ to} \\ 6 \times 10^{17} \end{cases}$
		† Soft steel	$\begin{cases} 6 \times 10^{17} \text{ to} \\ 6 \times 10^{13} \end{cases}$
Range	$10^2 \text{ to } 10^{11}$	Range	$10^{11} \text{ to } 10^{20}$

† During the first hour (500 to 3000 seconds) after twisting just within the elastic limits,

The limits here defined are somewhat arbitrary. They will be made more definite when a greater number of substances lying on the boundary between the classes have been examined. Information is lacking and particularly desirable in the neighbourhood of Andrews's critical temperature. From Table IX. it does not seem improbable that the critical temperature may be definable by a narrow limit of viscosity, quite apart from the substance operated on. What this limit may be I do not venture to assert, seeing that the viscosity of gases decreases on cooling, whereas that of liquids increases on cooling.

Table IX. gives the positively astounding range of variation of η , the chief variable of our material environment—a variable which throughout the whole enormous interval in question nowhere fails to appeal to our senses.

Phys. Lab., U.S. Geological Survey,
Washington, D.C., U.S.A.

XXXVI. *On the Effect of Permanent Elongation on the Cross Section of Hard-drawn Wires.* By Professors T. GRAY and C. L. MEES*.

IN the course of a series of experiments on the torsional rigidity of metals, forming part of the course of instruction in elasticity in the mechanical laboratory of the Rose Polytechnic Institute, we were somewhat surprised to find a

* Read before the Physical Society of Glasgow University, February 28, 1890. Communicated by Th. Shields, M.A., Secretary.

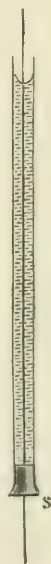
hard-drawn iron wire increased in total rigidity by being slightly stretched above its elastic limit. Slight changes in the modulus of rigidity, due to stretching, are of common occurrence ; but we had not previously noticed, nor heard of anyone else having noticed, such a change as to overbalance the effect of increased length and probably diminished section. The result seemed to make it probable that there was an actual increase of diameter produced by pull when the elastic limit is reached. As to whether actual permanent stretch is necessary to produce this effect we are not yet certain ; but there seems, from subsequent experiments, little doubt but that, for several metals, hard-drawn wires do expand laterally when they begin to take a permanent longitudinal set.

The observation here referred to seemed so interesting, that we instituted careful observations on the effect of slight stretching (that is to say, permanent stretching of from $\frac{1}{10}$ to $\frac{5}{10}$ of 1 per cent. of the original length) on the density of hard-drawn iron, brass, German silver, and pianoforte-steel wires. The results indicate that for an elongation of less than $\frac{1}{4}$ per cent. the section of the wire is slightly increased, above which the section diminishes. The experiment is, however, by this method exceedingly tedious and difficult, and hence the exact elongation which gives the greatest increase of section has not been determined. One or two of the results are quoted below mainly for the purpose of indicating the magnitude of the quantities concerned. These changes are very small ; and as they enter into the experiments on density determined by weighing in water as the differences between quantities of comparatively large magnitude, we cannot assume the results to be more than an indication confirmatory of the result obtained from the elasticity experiments. It may be remarked, however, that experiments on this subject were made by several members of the senior class both on soft and hard wires, with the consistent result that they obtained sometimes a gain, sometimes a loss of density for the soft wire, but always a loss of density in the hard wires. The specimens which showed most decided results were cut from two coils of very hard wire, one brass and the other German silver. The brass is so hard as to render it difficult to obtain permanent stretch without fracture. The results with iron and steel have not been quite so conclusive, owing to difficulties with oxidation during the density-determinations. A pianoforte-steel wire does, however, show signs of slightly increasing in volume just before breaking. The difference between the elastic strength and the rupturing strength is not great in pianoforte-wire, and it

is difficult to avoid fracture. We hope, however, to make a more systematic investigation, and to get over these difficulties by improved apparatus and methods of experiment.

Confining our attention to the brass and German-silver wires, the results indicate that if the stretch does not amount to more than from $\frac{1}{20}$ to $\frac{1}{10}$ of 1 per cent. the diameter increases. The elastic effect previous to the point where stretching is about to begin is for those wires in accordance with other well-known results of experiments on this subject, in so far as the diameter diminishes with increase of length; but we have not yet got a means of measuring with such accuracy as to give quantitative results as to the ratio of contraction to extension. The change from contraction to expansion seems to take place very near to the limit of elasticity, if not after that limit has been reached. A short distance beyond this limit contraction again sets in; and if the extension be as much as half of 1 per cent., the diminution of density, although noticeable, is not sufficient to produce increase in diameter.

The method of experiment which was used for the observations on which we base some of the above remarks on the effect of elastic stretch, was to pass the wire along the axis of a glass tube about 5 millimetres in diameter, which was hung on the wire in the manner indicated in the sketch by means of a rubber stopper *s*. The tube was then filled with water, and the position of the surface of the water read on a scale fixed on the back of the tube. The wire was then stretched and the fall or rise of the water observed. A diminution of volume was observed until the wire reached about the elastic limit, at which point the water rose, slightly indicating a swelling of the wire. We have made several attempts to increase the sensibility of the above arrangement by means of index-tubes fused into the side of the main tube, aided by narrow contractions in the tube, itself filled with mercury, from which the wire was protected at that point by a thin coating of shellac varnish. As yet, however, we have not been perfectly successful. The unstable condition of the mercury in the narrow contraction of the tube renders this method unsatisfactory. Should mercury-tubes prove superior, however, in experiments with iron and steel, we will platinize the other metals and use mercury.



The following are a few of the results obtained by the measurement of density before and after stretching, the

method being the determination of the loss of weight when immersed in water. Very careful precautions were taken to eliminate all trace of air from the wire and from the water by placing the vessel in the receiver of an air-pump and working the pump continuously for an hour or more. Care was also taken to minimize the effect of capillarity, and to correct for temperature in the measurements. Boiling the water by passing a stream of steam through it, causing a current to play on the wire, was also tried, with the result that the iron and steel wires tarnished too much to render the results of any great value. The effect of stretching was slightly diminished, a result which might possibly be due to annealing.

Kind of Metal.	Percentage permanent elongation.	Areas of section before stretching, in square centim.	Areas of section after stretching, in square centim.
Brass	0.10	0.01262	0.01268
	0.20	0.01261	0.01269
German-silver ...	0.12	0.008255	0.008300
	0.20	0.00827	0.00834

XXXVII. *On the Passage of Electricity through Hot Gases.*
 By J. J. THOMSON, M.A., F.R.S., Cavendish Professor of
Experimental Physics, Cambridge *.

GASES exhibit the most remarkable differences of behaviour with respect to the passage of electricity through them: the same gas under different circumstances may be either an insulator and require the electromotive intensity to exceed a certain value before any electricity at all can pass through it, or it may be a conductor and unable to insulate even a difference of potential as small as $\frac{1}{1000}$ of a volt (Blondlot, *C. R.* civ. p. 283). The study of the changes in the condition of the gas which accompany these remarkable changes in its electrical properties can hardly fail to afford most interesting information as to the method by which electricity passes through gases, and possibly through solids and liquids as well. As one of the simplest changes which can take place in the condition of a gas is that occasioned by a rise in tempe-

* Communicated by the Author.

perature, I have during the last year made a series of experiments on the changes which take place in the electrical properties of gases when they are heated.

Before describing these experiments I will sketch briefly the electrical properties of a gas, such as air, at the temperature of about 16° C. In order to get electricity through the air at atmospheric pressure, the electromotive intensity has to exceed 30,000 volts per centimetre; as the pressure of the air diminishes, the electromotive intensity required to produce discharge diminishes almost exactly in the same proportion. This goes on until the electric strength of the air reaches a minimum, after which any further diminution in the pressure causes the electric strength to increase; the pressure at which the electric strength is a minimum depending on the size and shape of the vessel in which the air is contained.

These results are, I think, in accordance with the view of the electric discharge through gases which I gave in the *Philosophical Magazine* for June 1883, and which, I think, derives great support from some of the experiments described below. According to this view, the provision of a supply of atoms by the splitting up of the molecules is the essential accompaniment of the electric discharge through gases. We may regard the atoms in the molecule as being in oppositely polarized states; one atom behaving as if it were charged with a quantity of positive electricity, the other as if it were charged with an equal quantity of negative. When the atoms are together in the molecule they neutralize each other's action at points outside the molecule, which behaves as if it were electrically neutral; but as soon as the atoms separate, since each one is essentially polarized, the gas acquires energetic electrical properties, and by the motion of its atoms electricity can be carried from one part of the gas to another. The ease with which the gas can be made to conduct electricity depends upon the ease with which its molecules can be split up into atoms.

Let us consider what, according to this theory, happens when a spark passes between two parallel plates. In some one or more of the molecules near the negative electrode the atoms separate, the positively charged atom goes to the negative electrode and the negative atom is repelled. If F is the value of the electromotive intensity between the plates, d the distance of the molecule which is ultimately split up from the electrode, the work done by the electric field on the positive atom when it reaches the negative electrode is Fde , where e is the charge on the atom; the work done in the same time on the negative atom will not be greater than this, so that the whole work done on the atoms in the molecule will not

be greater than $2Fde$. But if the molecule is split up by the electric field, the work done by the field must equal the difference between the energy of the molecule and its atoms, a constant quantity if the temperature remains constant. Thus Fd is constant, so that F must vary inversely as d . Now the effects produced by the collisions between molecules are probably so vigorous, that the electric forces trying to split up the molecules will have to commence their work afresh after each collision: in this case d is the free path of a molecule in the neighbourhood of the electrode, and the force required to produce discharge varies inversely as the free path and therefore inversely as the density. This investigation, or a similar one, will hold if we suppose that the splitting up of the molecules is helped by the presence of an "electric double sheet" near the surface of an electrode, corresponding to a definite difference of potential between the electrode and the gas, or whether we suppose *short* "Grothaus chains" to be formed, and the splitting up to pass from one molecule in the chain to another, being helped by the chemical forces between the molecules.

If we suppose the charges on the atoms to be the same as those deduced from electrolytic considerations, the force between the atoms in the molecule is so much greater than the force tending to separate them, in a field of 30,000 volts per centimetre, that it seems almost necessary to assume that the decomposition is helped in some such way as has just been suggested.

The increase in the strength when the density of the gas falls below a certain value may be accounted for by the diminution in the number of atoms available for carrying the electricity, by the interference of the vessel with the free path, and it may be by the increased difficulty of forming a "Grothaus chain" in a rare gas.

We ought also to notice that since Fd must be constant, and since d cannot be greater than the distance between the plates, the electric strength must be infinitely great when the distance between the plates is indefinitely small.

According to this view, the molecules of a gas are essentially electrically neutral, and any electrification in the gas must be due to the presence of free atoms. Now the most careful experiments seem to show that air is incapable of receiving a charge of electricity; for Nahrwold's experiments (Wied. *Ann.* xxxi. p. 448) show that apparent exceptions to this rule may be explained by the presence of dust, either originally present in the gas or given off from the electrodes.

Perhaps the most conclusive evidence of the impossibility

of communicating a charge of electricity to a gas in a normal state is afforded by Blake's discovery (*Wied. Ann.* xix. p. 518), confirmed by Sohneke (*Wied. Ann.* xxxiv. p. 925), that the vapour arising from an electrified liquid is not electrified.

The effect on the electric discharge of the disintegration of the electrodes seems to have been too much neglected. Metallic electrodes give off particles of the metal freely under many circumstances. Thus, for example, it has been known for a long time that they do so when they glow; and the recent experiments of Lenard and Wolff (*Wied. Ann.* xxxvii. p. 443) prove that they do so when exposed to ultra-violet light. Now a gas when exposed to ultra-violet light allows electricity to pass through it. This might either be due to the decomposition of the gas by the ultra-violet light (of which, however, there does not seem any direct evidence), or the discharge may be carried by the particles which the electrodes give off under the influence of ultra-violet light. The discovery by Wiedemann and Ebert, that electricity will not pass through the gas unless the cathode is illuminated, however brightly the rest of the field may be illuminated, points to this explanation; as Lenard and Wolff found that a positively charged plate does not give off particles of metal when illuminated, though a negatively electrified plate does so freely, and an uncharged one also, though not to so great an extent as a negatively electrified one.

Dr. Schuster has lately found (*Proc. Roy. Soc.* xlii. p. 371) that a gas through which an electric discharge is passing is unable to insulate the smallest electromotive intensity due to a source independent of that producing the discharge. This is easily explained on the preceding view; for the discharge splits up the molecules, provides a supply of atoms, and thus turns the gas into a conductor. In this case the atoms are supplied by the splitting up of the molecules by the electric field. There are, however, other ways of splitting up the molecules, of which raising the temperature is one; it is therefore interesting to study the effect of heat on the electrical conductivity of gases. The following experiments were made for that purpose.

Results of previous Experiments.

Previous experiments on the electrical conductivity of hot gases have given apparently conflicting results. Thus Becquerel, whose experiments have been confirmed by Blondlot, found that hot air conducted; while Grove could not detect any conduction between white-hot platinum wires sur-

rounded by steam ; and neither Maxwell nor Hittorff could find any trace of conduction through hot mercury-vapour. I have repeated all these experiments and verified the results. Hittorff found, too, that the conductivity of a flame was very much increased by putting volatile salts, such as the chlorides of sodium and potassium, into it, and that the increase in the conductivity depended on the nature of the salt.

Methods of Experimenting.

I have used three different methods of investigating the conductivity of hot gases, as the method which is the most convenient for one gas is not always so for another. In all these experiments the conductivity of the gas was sufficiently large to enable the current sent through a centimetre or two of the gas by a few Daniell's cells to be easily measured by a galvanometer of about 4000 ohms resistance. The galvanometer method, when available, is much more convenient and easy to use than the much more delicate one in which a leak through the gas is detected by an electrometer. Whatever method is employed it is essential that the current measured really passes through the gas, and is not due to the defective insulation of the electrodes which carry the current into it. The effective insulation of these electrodes requires considerable care, because no substance is known whose insulation can be trusted even at temperatures very much lower than those used in these experiments. It is therefore necessary to keep the places at which insulation is essential quite cool. The only really effective way of doing this is to keep such places well away from the hot gas and well screened from currents of hot air. In the following experiments this was done by making the upper part of the electrodes pass through vertical glass tubes, to which two long horizontal pieces of glass tube were fused; these pieces were about 8 inches in length, and were supported at the ends away from the electrodes by passing through holes drilled in solid pieces of ebonite, supported by retort-holders. These pieces of ebonite remained cool even when the gas had been kept at a white heat for some hours, and though they were tested repeatedly they were never found to leak. The electrodes were connected with the battery by long overhead wires insulated by pieces of sealing-wax placed so far from the hot gas that they never became appreciably warm.

In the greater number of experiments the gas to be investigated was contained in a platinum tube made by Johnson and Matthey. It was 7 inches long and 1 inch in diameter. Into this

tube the terminals insulated in the way just described dipped. The platinum tube was wrapped round with asbestos tape, then placed in an iron tube, and the whole arrangement put into one of Fletcher's muffle-furnaces, fed by 1-inch gas-pipe and a large air-blast worked by bellows such as are ordinarily used for forges.

If the substance experimented on was solid or liquid at ordinary temperatures, the gas was produced by dropping the solid or liquid into the tube and allowing the vapour from it to drive the air out; if the substance was gaseous at ordinary temperatures, a stream of it was conducted through the stem of a clay tobacco-pipe to the bottom of the tube and allowed to run until it had driven the air out.

The method of procedure was very simple. The electrodes in the tube were placed in series with the galvanometer and with a large Daniell's battery arranged in boxes with twelve cells in each; a reversing-key was placed in the circuit. When the gas had reached the requisite temperature, the supply of gas to the furnace was stopped, the battery put on one way, and the deflexion of the galvanometer read; the battery was then reversed and the deflexion again read. Though the deflexions are given in some cases the results must be considered as qualitative rather than quantitative, as the temperature was only fixed by describing the glow from the tube as dull red, bright red, yellow, bright yellow, and white.

It was found as soon as different gases were tested that they differed enormously in their power of acquiring conductivity by heating. Some of them, such as air or nitrogen, only acquired it to a very small extent; and I shall afterwards give reasons for believing that most of this can be accounted for by convection-currents produced by the disintegration of the electrodes. In other cases, however, notably for hydriodic acid gas, iodine vapour, bromine vapour, the vapour of sodium chloride, hydrochloric acid gas, the vapours of sodium and potassium, the gas acquired very considerable conductivity when the temperature exceeded a red light; so much so in fact that at a white heat two or three Leclanché cells were sufficient to throw the light reflected from the galvanometer-mirror right off the scale. The difference between the conductivity for the two classes of gases is so great that it suggests that the method by which the electricity is conveyed from one electrode to the other is not the same in the two cases.

It ought to be mentioned that even in the case of those gases which conduct best, there was not sufficient conductivity to produce a current that could be detected by the galvanometer until the electrodes began to glow; and from some

experiments which I shall describe later I am inclined to think that in order for the electricity to get with ease from the gas to the electrodes the latter must be glowing (and therefore disintegrating?).

The results obtained by using the platinum tube are given in the following table. The results for metallic vapours are not given here, as with this arrangement the temperature could not be raised high enough to volatilize many metals, so that a different method had to be used for these.

Substance.	Behaviour when heated to a yellow heat.
Air	Small deflexion, about 10 or 12 divisions for 156 Daniells.
Nitrogen.....	Much the same as air.
Carbonic acid	Rather less than air.
Ammonia	Rather less than air.
Steam.....	Considerably less than air.
<i>Hydrochloric acid</i>	Large deflexion; spot driven right off scale by 12 Daniells.
<i>Hydriodic acid</i>	Very large deflexion indeed; larger than for HCl.
Sulphuric acid	Small deflexion; very little more than air.
Nitric acid	About the same as air.
<i>Iodine</i>	Very large deflexion; comparable with HI.
<i>Bromine</i>	Large deflexion.
<i>Potassium iodide</i>	Conducted fairly well, but not so well as HI, HCl, or I.
<i>Sal-ammoniac</i>	Conducted well.
Sulphur (surrounded by nitrogen).	Small deflexion.
Sulphuretted hydrogen (ditto)	Very small deflexion until the temperature was raised to a white heat.
Mercury.....	Very small deflexion indeed; much smaller even than air.
<i>Sodium chloride</i>	Large deflexion.
<i>Potassium chloride</i>	Large deflexion.

In this table the gases which conduct well are printed in italics. Several of these are known to dissociate at high temperatures; thus iodine and bromine are known to do so to a very large extent, and the dissociation of the vapour of hydriodic acid, perhaps the best conductor in the list, is rendered very striking by the change in the colour of the vapour, which is brown at low temperatures and purple at high. There are, however, many substances in the list whose dissociation has not been observed, and in some cases cannot be great: thus the experiments on the vapour-density of

hydrochloric acid at high temperatures, and Scott's determination of the vapour-density of KI, show that there cannot be any very great amount of dissociation for these substances. I thought, however, it would be interesting to test whether or not there was any dissociation of the KI and HCl, since they conducted electricity when raised to a red heat. The potassium iodide was tried first. The stem of a long clay tobacco-pipe was placed in the platinum tube, one end reaching down to the bottom (the hottest part) of the tube, the other end connected by a glass tube with a bulb filled with a solution of starch; another glass tube was fixed on to this bulb and connected with a water-pump, so that when the pump was working, the gas from the bottom of the platinum tube bubbled rapidly through the starch solution: it thus passed very rapidly from a very hot to a cold place, so that if any dissociation took place in the platinum tube the constituents might not have time to combine before passing through the solution, where the presence of free iodine would be detected. On trying the experiment, a very distinct blue coloration of the solution was obtained, though no such coloration was produced by driving hot air through the bulb just before the KI was put in the platinum tube. The experiment was repeated several times, always with the same results; and we may therefore conclude that free iodine was present, in other words, in the KI which conducted the electricity there was dissociation.

A similar experiment was then tried with the hydrochloric-acid gas, the only difference being that the bulb now contained a solution of starch and iodide of potassium instead of a solution of starch alone. If the HCl is dissociated into H and Cl, and if these gases can be withdrawn from the hot platinum tube so quickly that they have not time to recombine, on bubbling through the solution the free chlorine will set free iodine from the potassium iodide and produce a blue coloration of the solution. On trying the experiment, the solution began to change colour as soon as the gas commenced to bubble through, and in less than a minute became almost black. This was not due to any oxide of nitrogen, because the coloration did not take place when air from the bottom of the hot platinum-tube was sucked through the solution, nor was it due to any impurity in the hydrochloric acid, for it did not occur when the HCl was allowed to bubble through the solution without being heated.

A similar experiment was tried with NaCl, and free chlorine was found in the hot vapour of this gas, though the effects produced by it were not so large as in HCl, where the solution

became black at once. Sal-ammoniac, another good conductor, is known to dissociate into ammonia and hydrochloric acid. In fact, whenever a gas became a good conductor when heated, I was able to detect dissociation by purely chemical means.

The converse statement is not, however, true; there are many cases in which dissociation takes place without the gas acquiring the power of conducting electricity. Thus, take the case of ammonia; this at high temperatures is known to dissociate into nitrogen and hydrogen; but ammonia heated to a temperature above that of dissociation, the dissociation being proved by the absence of any effect on litmus-paper of the hot gas rising from the tube, was an excessively bad conductor, being worse than air. Again, steam at high temperatures dissociates into hydrogen and oxygen; but steam even at these temperatures does not conduct electricity. The dissociation of the steam which would not conduct was proved by sucking the hot gases quickly from the platinum tube; when a series of electric sparks were passed through the gases thus sucked over, a large condensation took place.

There are, however, two kinds of dissociation—the one where atoms or unsaturated bodies are produced, as in the dissociation of iodine, bromine, chlorine, hydrochloric acid, hydrobromic acid, and hydriodic acid; the other where a complicated molecule is merely split up into simpler molecules, as for example ammonia, which at temperatures below that at which the molecules of nitrogen and hydrogen dissociate, dissociates into nitrogen and hydrogen *molecules*; or steam, which at temperatures below that of the dissociation of hydrogen and oxygen dissociates into *molecules* of these gases.

It is the first kind of dissociation which is always accompanied by conduction, while the second kind has little if anything to do with it. This is just what we should expect if we accept the view of the passage of electricity through gases given above, for in the first case we have the charged atoms which can carry the electricity, while in the second we have merely neutral molecules which have no such power.

[To be continued.]

XXXVIII. *On an Apparatus for the Distillation of Mercury in a Vacuum.* By WYNDHAM R. DUNSTAN, M.A., F.C.S., *Professor of Chemistry to the Pharmaceutical Society of Great Britain,* and T. S. DYMOND, F.I.C., F.C.S.*

[From the Research Laboratory of the Pharmaceutical Society.]

DISTILLATION of impure mercury constitutes the best method of removing foreign metals, and distillation in a vacuum is the only feasible plan of conducting the operation in the laboratory. It is doubtful whether mercury can be completely freed from zinc by distillation, and it is therefore safer to remove this metal, before distillation is resorted to, by agitating the mercury with warm concentrated hydrochloric acid.

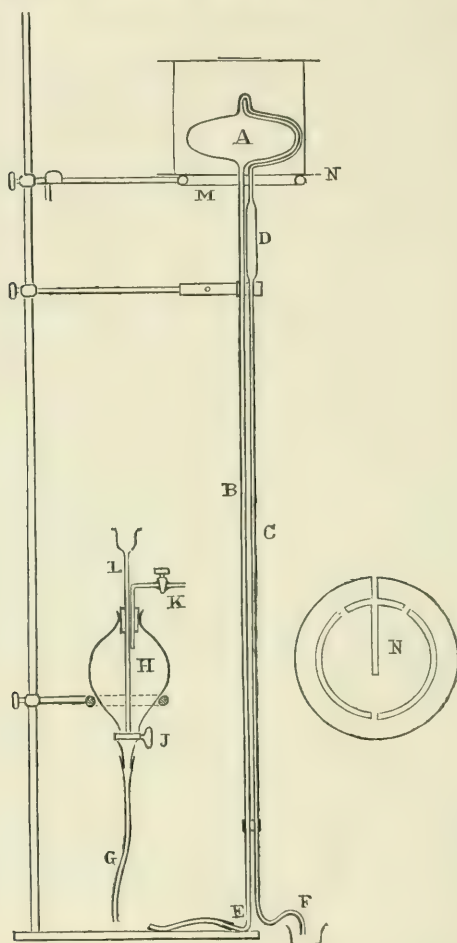
Different forms of apparatus for distilling mercury in a vacuum have been described by Weinhold, Weber, Wright, and Clark. The action of these different pieces of apparatus is primarily dependent on the same principle, but that described by Clark (*Phil. Mag.* 1884, xvii. p. 24) is undoubtedly the most convenient and is the form which is ordinarily used. It possesses, however, several disadvantages. It is inconveniently long, being at least 5 feet in length, and needs a special place in the laboratory where it must be permanently fixed. Moreover the apparatus is only applicable when a comparatively large quantity of mercury is available, since at the conclusion of the operation there remains in the apparatus between one half and one quarter of a litre of undistilled mercury, the amount being chiefly dependent on the diameter of the distillation-tube. To this residue more mercury must be added before distillation can be recommenced.

The still we are about to describe does not entail these disadvantages. It is easy and inexpensive to construct, and when once started is automatic in its action. It is rather more than a metre long, and when required for use can immediately be clamped on a retort-stand and may be as readily dismounted again. The residue of undistilled mercury which remains in the apparatus is less than 20 cubic centimetres.

The apparatus is constructed in the following manner:—A bulb A is blown on one end of a piece of thick-walled soft glass tubing B, and is made to assume somewhat the shape of an oblate spheroid, so that nearly the whole of the mercury may be distilled out of it. The other end of the tube has a small

* Communicated by the Physical Society: read March 7, 1890.

elbow-bend to admit of its connexion with the reservoir H by means of the stout rubber-tubing G. The diameter of the bore of this glass tube is 3 millim., and its length 1 metre, measured from the point at which it joins the bulb to the bend at the other end. To the summit of the bulb is sealed



a piece of tubing which is bent round one side of the bulb and terminates in the limb C, which acts as a Sprengel pump. The length of the tube from the lower surface of the bulb to the bend at its other end is about 1 metre, and the bore has a diameter of 1.5 millim. The upper part of this limb, at a dis-

tance of about 5 centim. from the bulb, is expanded to form a chamber D for the condensation of the mercury vapour; this chamber is 1 decim. long and 1 centim. wide. The other end of the limb is for convenience bent twice at right angles F, and beneath it is placed a receptacle for the distilled mercury. The movable reservoir H, attached by means of at least 1 metre of stout rubber-tubing, known as "pressure" tubing, to E is a large tap-funnel having a capacity at least twice as great as that of the bulb A. It is provided with a tightly-fitting indiarubber cork carrying a small tapped tube K, which projects just below the cork, and a thistle-funnel L which extends to the bottom of the reservoir. The apparatus is supported by a clamp immediately below the chamber D, and it rests on the bend E of the stout limb B.

Before the still is set in action it must be thoroughly dried. The reservoir H is then filled with dry mercury and raised until the liquid has ascended to the summit of the bulb A, and has commenced to fall over into the limb C. The reservoir is now slightly lowered, and by means of the tap J the flow of mercury is checked until it falls only moderately fast (as in a Sprengel pump) down the limb C. In about five minutes the chamber D will have been exhausted of air. As soon as the sharp "click" of the falling mercury is heard and the descending column in C is almost continuous, the reservoir is lowered until the bulb A is about half full. The reservoir H is now adjusted to act automatically in maintaining a constant level of mercury in the bulb A. The stopcock J having been shut, the bulb is heated and the distillation allowed to proceed for about half an hour until the vapour-pressure of the mercury for the maximum temperature to which the bulb will be raised has been attained. Air is then sucked out of the tube K until bubbles pass up through the mercury, when the tap in K is instantly closed. The tube of the funnel L now contains no mercury, the pressure of the air and of the mercury in the reservoir being exactly equal to the atmospheric pressure acting through L. The level of the mercury in the reservoir must now be adjusted until the surface of the mercury in the bulb is distant from the bottom of the reservoir (above J) by the height of the barometric column less the vapour-pressure of mercury for the temperature at which distillation occurs. This temperature having been ascertained, the adjustment may be made after direct measurement of the mercurial column. It may also be effected perhaps more readily by raising the reservoir little by little until on momentarily opening the stopcock J air is observed to bubble through the mercury. As soon as this occurs, the stopcock J is left open. The mercury from the

reservoir H will now be automatically supplied to the bulb A. As the mercury distils out of the bulb more rises from the reservoir to take its place, and air enters from the funnel L and bubbles through the mercury in the reservoir into the closed space above. Through this action of the reservoir the level of the mercury in the bulb will remain the same until the whole of the mercury contained in the reservoir has been distilled.

In order to heat the bulb A the tubes just below it are surrounded by the ring-burner M, which may be a circular piece of metal or glass tubing perforated at regular intervals with small holes; the flames proceeding from these perforations should be very small, and must on no account be allowed to impinge on the bulb or on either of the tubes. The bulb is now enclosed on all sides so that a hot air-chamber may result. This is best done by cutting a circular disk N, whose circumference is somewhat greater than that of the ring-burner, out of asbestos millboard, incisions being made to correspond with the tubes so that the disk may slide under the bulb and rest on the burner itself. On this disk as a base a cylinder of the same material, or of glass, is placed, the cylinder being wider and taller than the bulb. The cylinder is closed at the top by a rather larger and circular piece of asbestos millboard, in the centre of which a small round hole should be cut. By partially or entirely covering this hole with a small disk of millboard, it is easy to regulate the admission of air to the chamber. The cylinder is prepared from the millboard by thoroughly wetting it and rolling it round a bottle or wooden block of the proper size. When dry the cylinder is removed and secured by twisting a piece of thin copper wire round it. The bulb is thus heated in the air-chamber, and not by direct contact with the flames, and the bulb is effectually protected from the disastrous effects of draughts of cold air.

The temperature of the air-bath when distillation is proceeding ranges between 200° and 300° C. Since fresh mercury is automatically supplied to the bulb the still requires no attention, and may safely be left at work day and night provided that the gas pressure is almost constant. This may of course be ensured by fixing a gas-regulator in the air-bath. We have found, however, that an ordinary Sugg's dry governor introduced between the gas supply and the burner answers the purpose sufficiently well.

When the still is started for the first time the air-film on the glass is detached and passes away down the limb C. The distillation consists in continuous evaporation from the liquid surface unaccompanied by actual ebullition, or by the

“bumping” and spirting which are so noticeable when mercury is distilled under the ordinary atmospheric pressure.

The rate of distillation is mainly dependent on the capacity of the bulb A. We have generally worked with a bulb rather smaller than that described above, because it is easier to blow it of sufficient thickness. As the still is automatic in its action and needs no attention the quick distillation of a large quantity of mercury is not a point of much importance. It has frequently happened that the distillation has come to an end during the night, both the reservoir and the bulb being discovered nearly if not quite empty. This, however, has occasioned no inconvenience; it is only necessary to introduce more mercury into the reservoir and from thence into the bulb. This can be done without extinguishing the burner. The stopcock J is closed and the tap K is opened. Mercury is then poured through the funnel L. The stopcock F is now opened very gradually, so that cold mercury may not suddenly rush against the hot glass, until the bulb is half full, when the stopcock J is closed again. A piece of rubber-tubing is now attached to K, and air is sucked out until bubbles begin to rise through the mercury in the reservoir, when K is shut; after the lapse of about half an hour the stopcock J is opened. When a distillation has been finished and the apparatus is not further required for the present, it may be left standing with the stopcock J closed, and the end F dipping into mercury or otherwise sealed; it can then be started again at any moment. To empty the still, F is closed and the apparatus is carefully tilted so that the mercury remaining in C may flow into the chamber D. If now the end F be cautiously unclosed air will enter the apparatus through the empty limb C.

When this apparatus is at work in a dark room the remarkable phenomenon of the “flashing” of mercury is observed. It is seen in the condensation-chamber D. As the mercury liquefies flashes of green light are produced, which exhibit the spectrum of mercury. It would seem that this is an electrical effect arising from friction between mercury and glass. We have noticed that it is enormously intensified when one of the dischargers of a Wimshurst machine is brought near the chamber D. Under these circumstances the entire chamber becomes illuminated with a magnificent green light.

The apparatus may also be conveniently employed for observing the electrical discharge through mercury-vapour at different temperatures. For this purpose the ascending column of mercury in B and the descending column of mercury in C are used as electrodes. One terminal from the coil dips into the mercury in the reservoir H, the other into the

distilled mercury which has collected in the receptacle under F, and below the surface of which the extremity of the tube C is immersed.

We are now making observations on the character of the discharge which occurs under these conditions, in the absence of any foreign metal.

XXXIX. *Notices respecting New Books.*

Transactions of the Edinburgh Geological Society. Vol. VI. Part 1. 8vo. Edinburgh: 1890.

I. **MR. RALPH RICHARDSON, W.S.**, in an Inaugural Address gives a detailed and at the same time a comprehensive view of "Darwin's Geological Work," and warmly insists on the good results of his researches and published views: and he appends a list of Darwin's geological writings. II. "The Classification, Determination, Distribution, Origin, and Evolution of the Normal Micas," is the title of a paper by Mr. A. Johnstone, F.G.S. He arrives at the conclusion that—as the mica in recent igneous rocks is almost always *biotite*, and that this must therefore have been a product of igneous fusion,—and, as the micas of the older rocks are referable to *biotite*, *hydrobiotite*, *muscovite*, and *hydromuscovite*, the first may be safely considered as the original mica, and the others as varieties derived from it by water, CO_2 , and other natural agents. III. The supposed High-level Shell-beds in Easter Ross are shown by Mr. Hugh Miller to be only recent mussels and limpets thrown out on the blown sand which has now invaded the village. IV. Mr. John Henderson treats of "The Succession of the Lower Carboniferous Series to the West of Edinburgh, with special reference to the district around Cramond." This is in continuation of former researches, and is to be followed by remarks on higher beds in a future paper. V. "An Old Man and Woman; or Human Bones in a Serobicularia-bed at Newton Abbot, Devonshire," are described by W. Pengelly, F.R.S., in a paper of remarkable perspicuity and interest, every point of observation and treatment being well and clearly dealt with. The conclusion arrived at is that "the man and woman represented by the relics under notice were as old as the era of the deposition of the Raised Beaches of Devonshire, and therefore older than the period of their upheaval; but for this we are by no means unprepared, as the mollusks of the said beaches limit them to a Post-glacial age; and the caverns of the neighbouring Torbay district have undoubtedly established for Devonshire Man a very early Post-glacial, if not, as I believe, a Pre-glacial Antiquity." VI. "Improvements in the Methods of determining the Composition of Minerals by Blowpipe-Analysis," by A. Johnstone, F.G.S., is a very careful mineralogical paper, treating of the improved and newest methods and results, as more particularly set forth under the headings (A-J) in Tables of the operations of qualitative blowpipe-analysis at pages 47-52. VII. This is the Anniversary "Address on Recent Progress in

Palæontology as regards Invertebrate Animals," by Prof. H. A. Nicholson, M.D., D.Sc., F.G.S. After pointing out the false position taken by those who would suppress Palæontology as an independent branch of Biology, he proceeds to mention the discovery of the probably Foraminiferal structure of some oolitic grains,—of the probable occurrence of Radiolaria in Ordovician chert of South Scotland, and of the possible proof of fossil Radiolarian deposits being of deep-sea origin,—of the recent advances in our knowledge of fossil Sponges,—of the Stromatoporidæ and the true Hydrocorallines,—of the true Coral groups and other Cœlenterata,—the Monticuliporoids also, and the fossil Echinoderms, Annelides, Crustaceans, Arachnides, Insects, and Polyzoa. The Brachiopoda and Mollusca proper are slightly touched on, except the fossil Pteropods, which are more especially treated of. In conclusion Dr. Nicholson states "that the ascertained facts of Palæontology indicate, with an ever-increasing clearness, the existence of some general law of Evolution, by the operation of which new forms of life have been successively introduced upon the earth. As to the precise *modus operandi* of this general law, Palæontology does not, in my opinion, at present afford a decisive answer. That one great factor in the process has been the operation of 'Natural Selection,' as explained and defined by Darwin, does not, I think, admit of reasonable doubt. That 'Natural Selection' has been the *sole* agency at work is, however, a different and more doubtful point; and Palæontology, at any rate, does not seem to me to be yet in the position to supply the final solution to this most difficult and complex problem."

XL. Intelligence and Miscellaneous Articles.

ON ELECTRICAL VIBRATIONS IN STRAIGHT CONDUCTORS.

BY PROF. J. STEFAN.

THE distribution of a constant electrical current in a conductor, or its branching into several conductors, takes place in such a manner that, for the same strength of the total current, the disengagement of heat, according to Joule's law, is a minimum. This principle has been demonstrated by Kirchhoff for conductors of any given shape. It holds, however, only when the individual parts of the conductor contain no special electromotive forces; it does not hold therefore for variable currents in which inductive actions occur in the conductors.

In currents of rapid variability, particularly with periodical currents of very high number of vibrations, the influence which the resistances exert on their regulation becomes less in comparison with those of the inductive actions; and with periodic currents to the greater extent the higher the number of vibrations. In solving many questions relating to the behaviour of such currents we can entirely neglect the resistance of the conductors, and can use equations which hold for currents in conductors without resistance. G. Lippmann was the first to direct attention to these equations and their application.

Phil. Mag. S. 5. Vol. 29. No. 179. April 1890. 2 F

From these equations we may deduce the following principle:—The branching or distribution of a variable current takes place in such a manner that for any time its electrodynamic energy is a minimum for the same magnitude of the total current. As this energy may also be represented as a magnetic one, which has its basis in the magnetization of the conductor and of the medium surrounding it, the principle may also be so expressed. The distribution of the current takes place in such a manner that for the same magnitude of the total current its magnetic energy is a minimum.

In a straight conductor of circular section, which is exposed to no lateral actions, electrical currents can only be symmetrically arranged about the axis. In whatever manner the density of the current may vary from the axis towards the surface, the external magnetic action of the conductor is the same as if the entire current was concentrated in the axis. The minimum of magnetic energy is determined, therefore, by the fact that this energy has the smallest value in the space occupied by the conductors. This smallest value, and indeed the value zero, is attained when the entire current is condensed in an infinitely thin layer on the surface of the cylindrical conductor, for such a current-tube has no magnetic force on the space enclosed by it.

If the section of the conductor is not circular there is also a distribution of the current on the surface which makes the magnetic action at any point in the interior equal to zero, and corresponds to the minimum of magnetic work. This distribution is conformable with that which an electric charge acquires when it is on the conductor in a condition of equilibrium. Just as the resultant of the electrical forces of such a charge is zero at any point of the conductor, this is also the case with the resultant of the various current-filaments lying in the surface, if the density of the current along the periphery varies in the same manner as the density of the statical electrical charge. If, for instance, the section of the conductor is bounded by an ellipse, the densities in the various points of the ellipse will be as the perpendiculars which fall from the centre on the tangents to these points.

In his last published experiments H. Hertz has given very striking proofs that electrical vibrations of very high frequency can only move along the surface of the conductor. It also follows from his observations on such movements in band-shaped conductors, that the density of the current at the edges of the band is far greater than that in the middle of the broader side.

It may here be observed that the principle of distribution propounded not only serves for estimating the deportment of vibrations, but may also be applied to rapid electrical impulses, such as lightning-flashes, or constants of very short duration.

The velocity with which electrical waves travel in a conductor depends on the product of two factors—the coefficient of self-induction, and the capacity, both referred to unit length of the conductor. With the distribution of the current-density on the surface of a conductor, described above, the magnetic energy, and

therefore also the self-induction, is independent of the magnetic nature of the substance. In consequence of this, electrical waves of high periods travel in an iron wire with the same velocity as in one of copper. According to an experiment made by Hertz this, as a fact, is the case. Hertz explains this by the assumption that the magnetism of iron cannot follow such rapid vibrations. According to what is here stated the matter is much simpler: the iron remains free from any magnetic action of these vibrations.

From the experiments of H. Hertz, it results that the propagation of electrical waves in thin and thick wires takes place with the same velocity. According to the distribution of such waves on the surface of a conductor, it follows that this velocity in a straight conductor is independent, not only of the magnitude, but also of the form of the section. The coefficient of self-induction may be expressed by twice the potential of the electrical charge on itself divided by the square of the quantity. If in calculating the potential of the current we take the formula propounded by Neumann for the potential of two elements of current, this, in a straight conductor in which only parallel elements occur, reduces to the potential of two elements of the statical charge. If now the current-density as well as that of the charge in the surface are divided according to the same law, the same calculation must be made to determine the two potentials. Both are in like manner dependent on the size and shape of the section; and accordingly the product of the coefficient of induction and the capacity, as well as the velocity of propagation of the waves, are independent of the size and form of the section. The identity in the form of the electrodynamic and electrostatic potential has the consequence that the distribution of the current on such conductors as are parallel, and not connected with each other, may be determined by the rules of electrostatics. Here the potential of a conductor, which is only evoked by the induction of the other, must be called zero.—*Wiener Berichte*, January 9, 1890.

ELECTRICAL VIBRATIONS IN RAREFIED AIR WITHOUT
ELECTRODES. BY JAMES MOSER.

Incited by the view of Heaviside and Poynting, that electrical vibrations penetrate into a wire from the surface, and influenced by Hertz's experiments with the wire cage*, the author has used rarefied spaces without electrodes as conductors in which electrical vibrations occur.

A glass tube which contained a gas of constant rarefaction was surrounded with a wider tube, and the rarefaction varied in this by means of the air-pump. The following results were obtained:—

(a) At the ordinary atmospheric pressure in the outer tube the inner tube becomes luminous.

(b) With a sufficient rarefaction of the outer tube the phenomenon is reversed; the inner tube becomes dark and the outer one luminous. Here there is obviously a screening action.

* Wiedemann's *Annalen*, xxxvii. p. 395.

In the course of the preceding research the rarefaction was pushed still further, and

(c) The outer tube was again dark, the inner one luminous; so that to the eye this third stage was like the first one.

The more perfect vacuum exerts therefore no screening action; it has lost the power of conducting the electrical current.—*Wiener Berichte*, January 9, 1880.

ON THE FORMATION OF OZONE BY THE CONTACT OF AIR WITH IGNITED PLATINUM, AND ON THE ELECTRICAL CONDUCTIVITY OF AIR OZONIZED BY PHOSPHORUS. BY PROFS. ELSTER AND GEITEL.

The authors sum up the results of their investigations in the following terms:—

(1) Incandescent surfaces of platinum ozonize the surrounding air, even when combustions are excluded.

(2) When air is ozonized by contact with moist phosphorus it is seen to conduct electricity in the same manner as the gases of flame do.

(3) It could not be found that this process of ozonization had any electromotive force, or that the air which had been subject to it had any unipolar conductivity.

(4) The mere presence of ozone already formed, as well as the production of clouds from ammoniacal salts in the vicinity of phosphorus, are not connected with the origination of the conductivity of the surrounding air, or at any rate only to a subordinate extent.—Wiedemann's *Annalen*, March 1890.

NOTE IN CONNEXION WITH DROPPING-MERCURY ELECTRODES.

BY J. BROWN.

In the *Zeitschrift für physikalische Chemie*, iv. p. 577, there is a reference by Prof. Ostwald to my paper on "Helmholtz's Theory of Mercury-dropping Electrodes," communicated to the Philosophical Magazine for May 1889 by Dr. Lodge, as secretary to the Electrolysis Committee of the British Association.

Prof. Ostwald, however, considers only one of my experiments, viz. that which deals with the current in a wire connecting the dropping mercury with the mercury resting on the bottom of the vessel containing the electrolyte in which the drops form. My experiment shows that this current varies in a direction inverse to the change of resistance of the electrolyte, and is therefore conducted by the electrolyte, and does not consist of charges carried down by the drops as assumed by Helmholtz.

It is perhaps unnecessary to refer to Prof. Ostwald's criticism further than to point out that his method of explaining away my conclusion is inconsistent with the fact brought forward by me, but apparently not considered by Prof. Ostwald, that the current flows just the same whether the drops fall into the resting mercury or not, provided they form in the electrolyte in contact with the resting mercury.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

MAY 1890.

XLI. *A New Form of Electric Chronograph.* By Rev.
FREDERICK J. SMITH, M.A., *Millard Lecturer in Mechanics
and Physics, Trinity College, Oxford*.*

[Plate IX.]

DURING the last two years a research has been carried on by me on the subject of the acceleration-period of explosions†. In order to deal with the time-measurements which arose out of the investigation, it was found necessary to devise a chronograph which would register a large number of events following each other after small periods of time. As the chronograph used in these experiments has been found to be of use in other branches of scientific work, viz. in determining the velocity of shot, and many physiological time-measurements, I beg to offer an account of its construction and use to the readers of the *Philosophical Magazine*. The instrument has been called the *Electric Tram Chronograph*, because the moving surface is carried upon wheels running on rails.

The instrument has, in common with other forms of time-measuring instruments, a moving plate on which traces are made by means of electromagnetic styli. In other respects it greatly differs from other forms of time-measuring instruments.

In order that an electric chronograph may be of general

* Communicated by the Author.

† Proceedings of the Royal Society, xlv. p. 451.

use, several conditions have to be complied with ; some of these are as follows :—

(1) The moving surface on which the time-traces are made should be both long and wide. It should be *long*, so that periods greatly differing in their duration may be recorded on the same surface close together. It should be *wide*, so that a large number of time-determinations may be made and compared side by side on the same plate.

(2) The experimentalist should be able to vary the velocity of the moving surface.

(3) The surface should so move that all the time-traces may be in straight lines, and the velocity of the surface should be uniform during an experiment. The necessity for uniform movement is forced upon one by the experience of the difficulty found in subdividing a tuning-fork trace as recorded by a pendulum-chronograph. When a time-record is made on a surface which is moving at a uniform velocity, the difficulty of accurately subdividing a single vibration at once disappears.

(4) The marking-points of the electromagnetic styli, actuated by springs, when released from an electromagnet, should make a sharp and definite mark ; also the time between the breaking of the circuit and the marking should be as short as possible, and it should be constant in value.

These ends have been attained in the following manner :—To a vertical carriage, running upon wheels, between two rails, a sheet of smoked glass is fixed. The carriage is impelled by means of a cord attached to a weight ; after the weight has acted upon the carriage through a certain length of fall it is arrested, and the carriage moves with the velocity it has attained : this velocity is found to be practically constant for the whole length of the trace. It will be noticed that this arrangement embodies the principle of the Atwood machine. It will also be noticed that the impulse given by means of the falling weight gives a maximum velocity at the point where its pressure is taken off. With respect to pressure given by a spiral spring, as used in the well-known shooter employed in physiological work, exactly the opposite of this takes place. The writing-points of the electromagnetic styli and the tracing-point of the tuning-fork are placed so as to mark the moving surface.

The distance between the markings of the styli is obtained in terms of the length of the vibrations of the fork : from this the time between two or more markings is determined. This will become clear from the consideration of the following detailed description of the instrument.

The rails.—Two steel rails, A B and C D, each 2 metres long (Plate IX. fig. 1), are attached to three cast-iron standards: two of these, M and N, are shown. Each standard is furnished with two levelling-screws. The upper rail is adjustable, so that it may be placed parallel to the bottom rail, and at a correct distance from it for the width between the wheels of the carriage. (The rails are slightly inclined from D to C.)

The carriage. E F, is built up of bars (which are not shown) so as to be both light and rigid. It runs upon three wheels, each wheel being carried on two steel points; the points are adjustable, so that the face of the carriage can be placed parallel to the plane of the rails. To the front of the carriage a sheet of smoked glass is fixed with clips and screws. The carriage is furnished with a catch which engages with a detent at H; by this it is held back against the pull due to the weight, W, until required to run past the styli. A projection at the back of the carriage engages with a leather brake-band.

The brake.—A band of leather, L, is fixed to the standard, M, and also to a strong spiral spring at the back of the upper rail: the projection previously mentioned rubs under the band and brings the carriage to rest without any concussion.

The weight.—A gut-band or cord, passing over the pulleys, Q, P, R, is fixed at G; it is provided with a small ball which engages with a fork fixed to the back of the carriage. The weight impels the carriage until it is arrested by contact with an adjustable table T; the carriage then runs on with the velocity acquired. The velocity is found to be practically uniform throughout the whole length of a time-trace. The cord, if free, has a velocity approximately double that of the driving-weight.

Electromagnetic styli.—These are shown at A A (fig. 2). An electromagnet of peculiar construction is mounted upon a brass plate, which carries a T-shaped lever; to this a writing-point of aluminium, mica, or parchment-paper is attached. The lever is held by the electromagnet, as long as a current is acting upon it, against the pressure of a spring: when the current is broken the lever rises and gives its marking. The electromagnet is so constructed and wound that its period of "latency" is exceedingly small, and also constant within close limits. By means of a flat rectangular spring the stylus is attached to a pillar furnished with a sliding-holder B: each stylus can be easily adjusted to a vertical line for experiments in which a large number of markings are required in succession.

The pillar-support.—It has been found that, unless the support of the styli is free from vibration, the trace produced by them is not worth much. The pillar used in connexion with

the instrument consists of a heavy iron casting, CC (fig. 2) fitted with a slide, B, the slide can be raised or lowered by means of a screw with a milled head, the styli are attached to the slide B. By raising the slide after each experiment a large number of traces can be made side by side, and by the addition of an extra carrier as many as 10 styli can be carried. The pillar can be rotated on a triangular base, which is supported upon three levelling-screws. The screws rest after the method of Sir W. Thomson, viz. in a hole, a groove, and on a plane, on the slab which supports the chronograph. The points of the styli are adjusted to the face of the glass by a screw S. A simple pillar, A', can also be used when only one set of traces is required.

The tuning-fork.—A tuning-fork T is carried upon a pillar, which slides upon a block in which a V-groove is cut; a screw-stop limits its position against the glass. The fork may be driven electrically, or it may be excited otherwise. In the experiments on explosions the fork was started by means of a wedge, which kept the prongs apart, being suddenly withdrawn by means of an electromagnet.

The latency of electromagnetic styli.—While going through a large number of papers upon investigations in which electromagnets were used for measuring time, it was found that in nearly all cases it had been assumed that the armature of an electromagnet was detached at the instant of the circuit being broken; also, that in two instruments of similar construction the armature was released at the same instant. Several electromagnets of chronographs were examined: in some cases, where much iron was used in the cores, the time between breaking and release of the armature was as much as 0.04 second; also two apparently similar shaped electromagnets with similar windings, equal currents being used, differed in their action by some hundredths of a second. The experiments showed in a very definite manner that some electromagnets were not to be depended upon for close and accurate work.

In order to produce an electromagnetic stylus free from these evils a large number of experiments were gone through on the relative proportions of the cores and their yoke, also upon the winding. It was found that the yoke should be made large as compared with the cores; the dimensions finally adopted were:—

Cores 2 millim. diam. ; 10 millim. long.

Yoke 20 millim. \times 5 millim. \times 5 millim.

The method of measuring the period of delay spoken of, which may be called the latency of the stylus, is as follows, it

may be taken as an example of the way in which the instrument is used (see fig. 3) :—A piece of warm glass is smoked over the flame of a paraffin lamp furnished with a wide wick ; it is then attached to the carriage, and the stylus to be tested is adjusted to the surface of the glass, also the tuning-fork is adjusted so that its writing-point lightly touches the glass ; an electric circuit is then completed through the break I (fig. 2), and the stylus prepared for giving a signal. The carriage is then brought slowly past the stylus, the result of which is that a vertical mark I H (fig. 3) is produced ; the carriage is then held back by the detent, the stylus is again prepared, by the armature being caused to touch the poles of the electromagnet, the fork is excited, and the carriage released : the markings K N M L and A B are then produced. The tuning-fork point is brought against the glass so that a straight line may be drawn by it, the intersections of this with the curved line determine the limits of any vibration. The length of the traverse I N, duly turned into time, is the latency of the stylus. Lines are drawn by a needle's point through the points I and N, cutting A B in E F ; the value of E F is then determined by means of a micrometer microscope, constructed as shown in fig. 4. In all cases of estimating time the fork is excited for each observation, the writing-point of the fork being placed vertically above the writing-points of the styli, so that the velocity of the moving surface is common to both the fork and the stylus. The needle-point for scribing the vertical lines is carried on a kind of dividing-engine. The styli are found to have a latency of almost perfect constancy, its value being 0·0003 second. The first stylus constructed by me, and used in the Physiological Laboratory of the University, was not proportioned as the later ones have been ; it was tested by Prof. G. F. Yeo, and his result published in the 'Journal of Physiology,' vol. ix. nos. 5 and 6, gave as a value of latency 0·00062 sec. The improved result, viz. 0·0003, has been arrived at by a careful selection of the iron used, and a modification of the winding of the bobbins ; by the reduction of the latency the marking is rendered much more definite and readable. The two facsimile tracings (fig. 5) show the nature of the markings of a time-trace of a slow explosive wave. $\dot{B}\dot{A}$ or BA equals 0·00227".

The micrometer-microscope is mounted on a bridge E F (fig. 4) attached to an inclined table A B ; it is carried by means of a slide, which permits movement parallel to the trace which is put under it ; the slide is moved by a screw having 40 threads to the inch ; the screw has a micrometer-head divided into 25 large divisions, each of these is again divided into 4 parts, so

that $\frac{1}{40} \times \frac{1}{100} = \frac{1}{4000}$ of an inch can be read with ease. The microscope is furnished with a fine fibre which is brought over the trace to be measured; a rod of rectangular section H K is attached to two links or rods, L H, M K; the links being equal and moving about the points M, cause the rod to move always parallel to itself; upon the rod the trace rests; any part of the trace can be brought under the microscope. The markings appear as rather wide lines of light; a V-shaped scale in the field of the instrument enables one to bisect these lines. Fig. 3 gives an illustration of its use. The centre of the field is brought over C, the index of the micrometer-screw being at zero; then the microscope is moved by the screw till the centre coincides with D. The length C D is then recorded, let it be L; then the micrometer is brought to zero again, and E is brought under the centre, and E F is then measured in the same manner as C D, let it be l ; then, if x denote the time of traverse over E F, and t the time of one vibration,

$$L : l :: t : x,$$

and

$$x = \frac{lt}{L}.$$

Fractions of a vibration can thus be easily estimated with great accuracy. This proportional method of subdividing the vibrations depends upon the fact that the velocity of the carriage is practically uniform.

The method of preserving time-traces.—After the smoked glass has received records of time-traces it may be preserved by being varnished. It is a somewhat difficult matter to cover a smoked plate with photographic varnish without making either streaks on the plate or removing a good deal of the carbon surface; but if the varnish be diluted with about 25 times its volume of strong methylated spirit, it may be poured over the plate without injuring the trace. When it has dried off ordinary photo-varnish may be applied without any risk of doing harm. In the first case the plate should be cold, in the second it may be a little heated before a fire previous to the application of the thicker varnish. The traces can then be used as negatives to print from in the usual way. Eastman's bromide-paper in rolls has been found to be most convenient for reproducing the traces. One of these is shown at fig. 5. The lines are thicker than those usually made, as a thicker deposit of carbon was used to get a very dense negative to make a print for this communication to the Philosophical Magazine.

I wish to add that Mr. A. W. Price has greatly assisted me in the manufacture of the new instrument. The method of increasing the velocity of the carriage by the introduction of a pulley attached to the driving-weight is due to him.

XLII. *On the Electrical and Chemical Properties of Stannic Chloride; together with the Bearing of the Results therein obtained on the Problems of Electrolytic Conduction and Chemical Action.*—Part I. *Experimental Observations.* Part II. *Theoretical Considerations.* By WARD COLDRIDGE, B.A., Scholar of Emmanuel College, Cambridge*.

INTRODUCTION.

THE germ from which this work has been developed was found in Faraday's statement that Stannic Chloride is a nonconductor. In the first instance this led to an investigation of the lower limit of its conductivity; the result which is here recorded was submitted to the Meeting of the British Association at Bath in 1888 by my friend Mr. W. N. Shaw, Fellow of Emmanuel College, who experimented with me on this point: in the second instance I examined the condition requisite for the development of electrolytic power; the results obtained are here for the first time recorded.

It is claimed that, by taking advantage of the suitable chemical and physical properties of stannic chloride, a definite advance has been made towards the resolution of the ambiguous statement that "heterogeneity is necessary for the development of electrolytic power," and that the results of Part I. throw light on the nature of an effective impurity, and in so striking a manner exhibit the parallelism between the chemical and electrical properties that the conviction arises of an ultimate explanation common to both. I have endeavoured to arrive at a single consistent view which shall explain the phenomena observed; and in stating the idea I have carefully abstained from wandering into disquisitions on other ideas, as that of Arrhenius's vagrant atoms, which, according to my notion of the stability of the fundamental chemical molecule, are untenable.

The field of research from which these results have been gathered is a fertile one. Incidentally some opportunities are mentioned: I am conscious that pure pentachloride of antimony, *inter alia*, would yield interesting results.

With much pleasure I acknowledge my indebtedness to

* Communicated by the Author

Professor J. J. Thomson, F.R.S., for the suggestion of examining the conductivity of the chloride at the boiling-point ; and to W. N. Shaw, Esq., as well for the use of his room at the Cavendish Laboratory as for the interest he has kindly evinced in my results ; and, lastly, to Professor Dixon, F.R.S., who has kindly read my manuscript.

Part I.—EXPERIMENTAL OBSERVATIONS.

Preparation of Stannic Chloride.—Stannic chloride was prepared by passing a current of dry chlorine gas over melted tin. The collected distillate was a yellow powerfully fuming liquid ; the yellow colour was due to an excess of chlorine, which was removed by allowing the liquid to stand for two days over granulated tin. After decantation it was distilled from a fresh quantity of granulated tin. The liquid then boiled at a perfectly fixed temperature of 112°C ., which is accurately the boiling-point observed by Andrews, and differs considerably from Dumas's value of 120°C . The liquid thus obtained is perfectly colourless : it exhibits a great attraction for moisture, combining to produce a white crystalline solid, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Lewy), insoluble in the chloride.

Electrical Conductivity of the Pure Chloride.—The conductivity of the pure stannic chloride was examined by placing it in a V-tube with platinum electrodes : in the circuit were included a high-resistance galvanometer (4000 ohms), and twenty secondary cells of electromotive force of 40 volts. On completing the circuit by depressing a key not the slightest effect was observable ; the insulation was absolute within these limits of delicacy, and was in marked contrast to the conductivity of a pencil-streak of black-lead on paper, for, with the latter in circuit instead of the former, the spot of light immediately moved off the galvanometer-scale.

In order to test whether the insulating power was appreciably affected by elevation of temperature, the containing V-tube was heated in a bath of aniline. But as the temperature rose to 20° , 30° , 40° , 100° , and even to the boiling-point when the stannic chloride was distilling freely—and this last observation is of particular import because the physical homogeneity of the liquid agitated now with bubbles of vapour has been disturbed—no conductivity could be observed. To arrive at some concept of the degree of insulating power, the following experiment was performed. The same galvanometer was placed in circuit with the resistance of one megohm and supplied with the electromotive force of one Daniell cell ; the deflexion then observed was thirty-five of the scale-divisions of the galvanometer. An electromotive force of

forty volts would give this deflexion through a resistance of forty megohms. Thus, then, the lower limit to the value of the conductivity of the above column of pure stannic chloride cannot be less than one thousand and six hundred megohms. There is thus in this chemically homogeneous liquid a high degree of insulating power, and one admirably adapted for the study of the influence on its electrical conductivity of the destruction of that homogeneity. The agents used to produce the required heterogeneity may be classified :—

- A. Dry gases.
- B. Liquids.
- C. Solids.

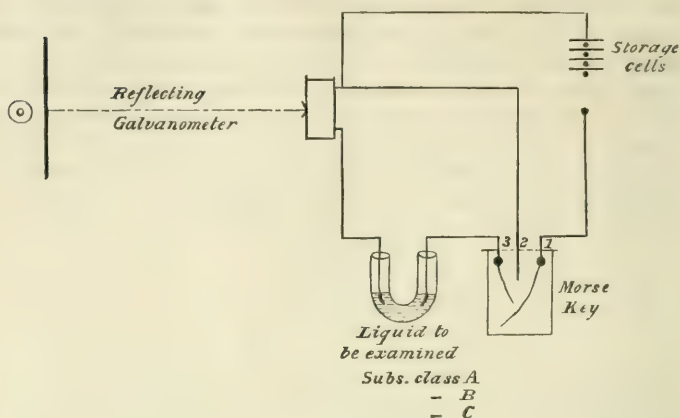
Class A. The Effect of Dissolved Gases on the Conductivity.

I. *Chlorine Gas*.—A specimen of stannic chloride of a yellow colour was prepared as above, save that the excess of chlorine was not removed by granulated tin. The experiments above described, using the yellow liquid with the excess of chlorine, were again performed, and precisely the same results were obtained ; so that the dry chlorine gas was without effect on the conductivity. It will suffice to note that no compound of tin and chlorine exists in greater proportion than one atom of tin to four atoms of chlorine.

II. *Dry Hydrochloric-Acid Gas*.—The hydrochloric acid was carefully dried by sulphuric acid. It was then passed for a quarter of an hour through a V-tube containing the tetrachloride. An absorption of the gas was indicated by the fall in temperature of the liquid through four to five degrees, which may, however, have been due to the evaporation of the stannic chloride, and on tightly corking both arms of the V-tube the liquid rose to different levels.

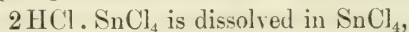
The accompanying diagram illustrates the arrangement of apparatus which I used both here and in subsequent experiments to detect the existence of a polarization effect. The battery used to electrolyse this tetrachloride saturated with hydrochloric-acid gas consisted of twenty-five storage-cells. On making the primary circuit, a small direct current passed, producing a deflexion of thirty scale-divisions. The cell had thus a resistance of above 5×10^7 ohms. Calculating from the magnitude of this direct current, it was not to be expected that a polarization-current would be observed : in fact, after passing the primary current for half an hour, no current was detected on making the secondary circuit.

Diagram of the Electrical Apparatus used in these experiments.

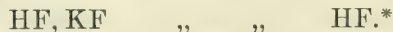


After resaturating the tetrachloride with hydrochloric-acid gas an increased conductivity was registered.

An additional experiment was then made to determine whether this conductivity was merely a residual phenomenon due possibly to the incomplete drying of the acid gas. But the same order of conductivity was observed on saturating a fresh quantity of the tetrachloride with the acid gas, which had been completely dried by sulphuric acid and a column of phosphorous pentoxide. Now the pure tin tetrachloride is at least a comparative insulator, and liquid hydrochloric acid exhibits the same property. Yet when dry hydrochloric-acid gas is dissolved in the tetrachloride, some conducting-power is developed. Now it is known that a compound, $2\text{HCl} \cdot \text{SnCl}_4 \cdot 6\text{H}_2\text{O}$ exists; and, further, compounds $2\text{NaCl} \cdot \text{SnCl}_4$, &c. are of frequent occurrence and of a common type; there can therefore be but little doubt that a compound, $2\text{HCl} \cdot \text{SnCl}_4$, is formed on passing the dry acid gas into the tetrachloride, and to the presence of this compound must the developed conductivity be due. The observed development is accurately analogous to that with which Moissan endowed liquid hydrofluoric acid by dissolving in it the freely soluble, thoroughly dried hydrogen-potassium fluoride. In the one case



in the other



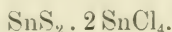
III. *The Effect of Dry Sulphuretted Hydrogen.*—Sulphuretted hydrogen was generated and washed in the usual

* *Comptes Rendus*, 1887.

way, and then thoroughly dried by the use of tubes containing calcium chloride and by a column of phosphorus pentoxide. The gas thus carefully dried was passed for an hour into the tetrachloride. The only alteration in appearance was due to the separation of some white crystals, resembling in appearance the hydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. After filtration the colourless liquid, which smelt strongly of hydrosulphuric acid, and fumed in the air as the original unaltered liquid does, was tested for conductivity. But within the limit of these experiments the conductivity was unaltered by the presence of the hydrosulphuric acid. In striking contrast with this result is the effect observed on merely placing a few drops of absolute alcohol on one of the platinum electrodes, shaking it until no more than a mere film adhered and then replacing it; a deflexion is immediately registered and stannic sulphide is formed on the electrode.

These observations at once raised a question of considerable chemical interest as to the nature of this nonconducting product: had there or had there not been chemical action? In Watts' 'Dictionary of Chemistry' the following statement is given on the great authority of Dumas:—

"Stannic chloride quickly absorbs sulphydric-acid gas, giving off hydrochloric acid, and forming a stannic sulphochloride,

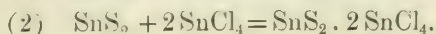
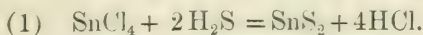


The compound obtained by the perfect saturation with sulphydric-acid gas is a yellowish or reddish liquid heavier than water. When heated it gives off SnCl_4 and leaves SnS_2 ."

This abstract is in accord with the account of Dumas's observations, given in Frémy's *Encyclopédie Chimique*. According to these dicta, the answer to the above question must be that there is chemical action. Assuming for a moment that the statement is categorically correct and complete, and that the liquid is indeed a chemical compound, $\text{SnS}_2 \cdot 2 \text{SnCl}_4$, then even this compound is a nonconductor. But this point is hardly worthy of expression; because the fundamental assumption, the existence of the liquid compound $\text{SnS}_2 \cdot 2 \text{SnCl}_4$ can be completely disproved. Attention was directed to the following points in the above statement:—

(a) "That sulphydric-acid gas is quickly absorbed and that hydrochloric-acid gas is evolved."

The idea is obviously that the following changes occur:—



(b) "The product is a yellowish or reddish liquid heavier than water."

It was noted that no mention is made of the white crystalline compound.

(c) "On heating the liquid, SnCl_4 is evolved and SnS_2 remains."

This observation as to the residue of stannic sulphide was verified, and beautiful specimens of the "mosaic gold" were obtained. But it should be noted that the liquid has been heated.

The following experiments were then made:—

(a) The fumes which are evolved on passing in dry hydrosulphuric acid smell strongly of the sulphuretted hydrogen even when the gas was slowly delivered, and immediately blacken moist lead-acetate paper: they are moreover acrid, and distinctly smell of the tetrachloride rather than of hydrochloric acid. But to establish the presence of the tetrachloride vapour, a test more reliable than the sense of smell was required. The following was devised:—A glass rod with a drop of water at the end was held in the fumes; after a minute, whilst the dry liquid below remained colourless and clear, here in the drop of water stannic sulphide was deposited. The fumes therefore contain the vapour of the tetrachloride and sulphuretted hydrogen, which are caused to combine by the action of the water. Thus, then, the statement that hydrochloric acid gas is evolved, if it be in the least degree positively true, is fatally incomplete.

(b) The liquid compound, the supposed stannic sulphochloride, was next distilled. The warming was gently regulated; as the temperature rose gradually to 50° , 60° , 70° , sulphuretted hydrogen was copiously evolved in such quantity that the liquid assumed the appearance of boiling, whereas distillation had not commenced. At 112°C. , the boiling-point of stannic chloride, a free distillation commenced, and the greater portion of the tetrachloride was thus recovered. Finally the temperature rose, a solid residue melted, and stannic sulphide remained, though, from a gravitation experiment, in less quantity than was required by the hypothetical constitution " $\text{SnS}_2 \cdot 2\text{SnCl}_4$." A veritable compound stannic sulphochloride could not at low temperatures evolve sulphuretted hydrogen copiously and then distil at the ordinary boiling-point of stannic chloride.

(c) The presence of the residue of stannic sulphide proved that, on passing dry hydrosulphuric-acid gas into the chloride and then subsequently heating, some reaction occurred. But the question remained as to how far this production of the

sulphide was a function of the temperature-change. Was its formation induced by the elevation of temperature? It was noticed that, on warming up the product obtained by passing the dry gas into the liquid, the white crystals dissolved and the liquid became yellow; there was thus a probability that these white crystals would prove the key to the change. Some of the crystals were separated and heated; they then evolved sulphuretted hydrogen, hydrochloric acid, and left a residue of stannic sulphide. But it still remained to examine whether the unheated saturated stannic chloride contained any stannic sulphide. This point was determined by evaporating the saturated liquid to dryness *without heating it*, an operation which could be effected by taking advantage of the volatility of the tetrachloride. A current of thoroughly dried air was steadily driven into the saturated tetrachloride: fumes of the tetrachloride mixed with sulphuretted hydrogen were evolved; but in the end, when all the liquid had disappeared, it was found that not a trace of stannic sulphide had been formed, and that in its place was a residue of the white crystalline solid. Therefore, then, dry sulphuretted hydrogen may be passed into the tetrachloride, and, if the temperature be not raised, not a trace of stannic sulphide is formed: by far the greater part there is no combination, to the smaller extent these crystals are formed. The transformation which these crystals undergo when heated fully explains the formation of the stannic sulphide observed by Dumas. The composition of these crystals was determined. A small tube was weighed and about ten grams of the tetrachloride were placed in it, and saturated with dry sulphuretted hydrogen; the liquid was then evaporated to dryness by a current of dry air. In this way, in two experiments, were obtained in the tube,

(1) 1.15 gram of the compound $\text{SnCl}_4, n\text{H}_2\text{S}$.

(2) .926 " " " "

The tubes were then carefully heated by a spirit-lamp. The solid melted and evolved sulphuretted hydrogen; and next, as the heating was continued, hydrochloric acid, and a residue of stannic sulphide to the amounts respectively,

(1) .48 gram,

(2) .365 ,,

which numbers correspond closely to the value $n=5$. These white crystals, which are the sole product of the action of dry sulphuretted hydrogen on stannic chloride, are thus $\text{SnCl}_4 \cdot 5\text{H}_2\text{S}$, analogous to $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

The reaction which occurs on heating is thus:—



The effect of adding a drop of water to these crystals is to produce stannic sulphide ; and this action is thus in harmony with that described above of holding the drop of water in the mixed vapours*.

Judging, then, from the fact of the unaltered boiling-point of the liquid, and from the analogy of $\text{SnCl}_4 \cdot 5\text{H}_2\text{S}$ to $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and from the fact that the former as well as the latter separates, the conclusion that the sulphuretted hydrogen is merely mechanically mixed with the chloride is strongly supported.

Class B. *The Effect of various Liquids on the Conductivity.*

I. *Chloroform*.—Chloroform was first taken because of the similarity of its chemical structure to that of stannic chloride.

The conductivity of chloroform was found likewise to be nothing within the range of these experiments. The tetrachloride mixes perfectly with the chloroform. In the first instance the proportions taken were two volumes of the former to one of the latter. The conductivity of this mixture was nothing. In the next experiment one volume of the tetrachloride was diluted with five of the chloroform. But there was still no conductivity.

In each instance the result was checked by placing a streak of black-lead on paper in circuit instead of the mixture.

There would seem *à priori* to be no chance of a reaction between so stable and saturated a compound as chloroform and stannic chloride ; as an experimental fact the mixture does not conduct. The test was applied of passing in dry sulphuretted hydrogen ; no precipitation of stannic sulphide resulted ; the behaviour was the same as if no chloroform had been present, and in marked contrast to the influence of water or absolute alcohol.

II. *Absolute Alcohol*.—Rectified spirit of good quality was dried by standing over lime and by subsequent distillation from lime. The phenomenon observed on adding a drop of this alcohol to stannic chloride is analogous to that which occurs when water is added. A white beautifully crystalline compound is formed and much heat is evolved. By adjusting the quantity of alcohol and cooling the vessel with water the whole of the liquid can be transformed into a mass of these crystals, which dissolve again on adding more alcohol. This alcoholate has probably the constitution $\text{SnCl}_4 \cdot 5\text{C}_2\text{H}_5\text{OH}$, as would be concluded from its analogy to the amyl alcoholate described by Bauer and Klein (*Zeits.f. Chemie* [2] iv. p. 370).

* My best thanks are due to the authorities of Exeter Grammar School, who placed their laboratories at my disposal during the Christmas vacation, and to my friend Mr. J. M. Martin, who helped me in the manipulation involved in the examination of the above change.

The solution of the alcoholate conducts with facility ; and that electrolysis is proceeding is shown by a polarization-effect of considerable magnitude. The electrolyte remains clear and colourless. There were no signs of an evolution of gas at the anode, and no tin was deposited at the cathode ; but the difference between the electrolyte before and after the passage of the current was shown by its behaviour towards an alcoholic solution of mercuric chloride. The unelectrolysed solution of the stannic chloride gave no precipitate of calomel, but that through which the current had passed at once precipitated calomel. In one experiment, when a concentrated solution of the tetrachloride was electrolysed for two hours, the whole was converted into a magma, and some of the solid adhering to the electrode when dissolved in alcohol gave the reaction for the stannous salt. In this experiment a copper voltmeter showed that a current of between $\cdot 1$ and $\cdot 15$ of an ampere had passed.

The production of calomel in the electrolysed solution shows that the current has transformed the stannic salt into a stannous salt, stannic chloride into stannous chloride. The absence of an evolution of chlorine gas is accounted for by the certain action of electrolytic chlorine on the alcohol.

Qualitatively it has been proved that alcohol added to stannic chloride induces such a condition of instability as to render it capable of electrolytic conduction. Moreover this power of electrolytic conduction is closely analogous to the power of sulphuretted hydrogen to precipitate stannic sulphide. Mention has been made of the fact that the placing of a mere film of absolute alcohol on one of the platinum electrodes produces in the stannic chloride saturated with sulphuretted hydrogen a slight conducting power and the precipitation of stannic sulphide. When more alcohol is added, there results a copious precipitation of stannic sulphide ; and when sulphuretted hydrogen is passed into the alcoholic solution of stannic chloride an immediate precipitation of stannic sulphide occurs.

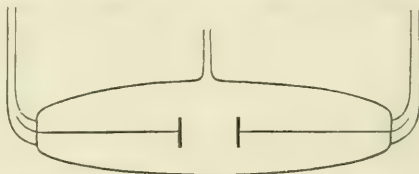
III. *The Effect of Dry Ether.*—Advantage was next taken of the curious fact that ether combines with stannic chloride to form a compound, $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, which is soluble in excess of ether. Absolutely dry ether was prepared in the usual way. On adding the ether to the chloride a mass of white crystals are formed, which are difficultly soluble in the ether at the temperature of the laboratory. Ether was added to the crystals and shaken ; the cell was then placed in circuit ; a deflexion of sixty scale-divisions was registered. But on concentrating the solution by placing the cell in warm water,

the conductivity improved and became comparable with that of the alcoholic solution.

After passing the direct current for thirty hours, a slowly diminishing polarization-current was registered producing at first a deflexion of thirty scale-divisions. The electrolysed product contained some stannous salt.

On passing dry sulphuretted hydrogen into the cold ethereal solution an emulsion is formed, and the tetrachloride separates at the bottom of the ether. The distinction between the action of ether and of alcohol under these circumstances will be adverted to in Part II.

IV. *Effect of Strong Aqueous Solution of Hydrochloric Acid.*—Instead of taking, as in the previous experiments, a V-tube for the electrolytic cell, a cell of the same pattern was used as that described and devised by Mr. Fitzpatrick (Brit. Assoc. Reports). It is a glass cylinder closed at the ends, where wires leading to the circular platinum electrodes enter; and midway between the electrodes there is an open tube fused into the cylinder. A drop of strong hydrochloric acid



was poured down the central tube on to the surface of the chloride: as long as it remained unmixed the effect was *nil*, but on admixture the cell conducted. The same E.M.F. was used as in B. I, II, III, viz. that of twenty-five storage secondary cells and a polarization-current of approximately 2×10^{-7} C.G.S. units, which is equivalent to a scale-deflexion of sixty scale-divisions. The act of mixing was accompanied by the evolution of heat and by the formation of a subsequently dissolved gelatinous substance. This reverse current was constant at the temperature of the room for nearly an hour: this constancy and its high E.M.F. led me to observe it at different temperatures. The primary current ran for three minutes; at a temperature of 31° the polarization-current gave a deflexion which diminished from 77 scale-divisions to 56 in the course of fifteen minutes; at a temperature of 41° it fell from 79 to 63 scale-divisions in twelve minutes; at 51° , from 79 to 55 in ten minutes; at 71° , some hydrochloric acid boiled off explosively; at 90° more was expelled, the polarization was weaker, and decayed from 55 to 0 scale-divisions deflexion at 96° C.

V. *The Effect of Absolute Alcohol on the Tetrachloride saturated with Sulphuretted Hydrogen.*—Incidentally, in describing the effect of sulphuretted hydrogen on the alcoholic and ethereal solutions of stannic chloride, I was compelled to state some of the results which would naturally have fallen under this heading. It has been recorded:—

(1) That stannic chloride saturated with sulphuretted hydrogen does not conduct.

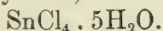
(2) That a mere film of absolute alcohol adhering to one electrode is sufficient to endow such a solution with some conductivity.

To amplify (2): the actual deflexion observed was forty scale-divisions. On pouring a little alcohol down one arm of the cell the conductivity increased so that a 150 scale-division deflexion was registered. Directly the alcohol reached the solution there was a vigorous interaction and stannic sulphide was precipitated. After a similar quantity had been added to the other arm and the cell shaken, the current through the galvanometer was sufficiently great to turn the mirror at right angles to its original position.

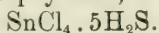
Class C. *The Effect of Solids on the Conductivity of the Tetrachloride.*

The endeavour to destroy the chemical homogeneity of the stannic chloride was a failure, owing to the insolubility of the solids that were tried. Attempts were made with

(1) The crystalline hydrate,



(2) The crystalline sulphhydrate,



(3) Dry sodium chloride.

(4) Moist sodium chloride.

(5) The double ammonium stannic chloride.

After failing to obtain other than a negative result with sodium chloride, it seemed possible that if the chloride of the alkaline metal was first combined with stannic chloride the double salt might dissolve. The success that Moissan enjoyed by adding to the liquid hydrofluoric acid, the double potassium hydrogen fluoride, suggested this attempt. Some quantity of the double ammonium stannic chloride, $(2\text{NH}_4\text{Cl} \cdot \text{SnCl}_4)$, was prepared according to the directions given by Bongartz and Classen (*Ber.* xxi. p. 290), who determined the atomic weight of tin by electrolysis a solution of this salt in the acid ammonium oxalate. The double chloride was perfectly dried by standing over phosphorus pentoxide in a desiccator. A gram of this dry salt was added to the stannic chloride in the V-tube.

The effect on the conductivity, even after heating to and at the temperature of 100°C. , was nothing. A drop of water added to the double chloride before adding it to the stannic chloride was powerless to promote conductivity.

The fact, then, is that neither the crystalline hydrate, nor sulphhydrate, nor moist nor dry sodium chloride, nor the moist nor dry ammonium stannic chloride have any influence on the conductivity of the stannic chloride. The solids remain outside the sphere of action: and, like the drop of strong hydrochloric acid as long as it was unmixed with the stannic chloride, and like the perfectly dissolved chloroform and the gases chlorine and sulphuretted hydrogen, having produced no effect on the chemical homogeneity of the stannic chloride, which remains stannic chloride, they were without influence on its electrical conductivity.

[To be continued.]

XLIII. *The Villari Critical Points of Nickel and Iron* *.

By HERBERT TOMLINSON, *F.R.S.*†

WE owe to Villari the discovery that the magnetic permeability of iron is increased by longitudinal traction provided that the magnetizing force does not exceed a certain limit, but beyond this limit the traction produces decrease of permeability so that for a certain value of magnetizing force, known as the Villari's Critical Point, longitudinal traction has no effect in either direction. Several experimenters have verified and extended Villari's discovery, notably Sir William Thomson and Prof. Ewing, but, as far as the author is aware, no observer has been as yet able to find a similar critical point for nickel. If, however, we confine ourselves to the consideration of the *temporary* magnetization‡, a Villari critical point in nickel can be detected with comparative ease. In the present investigation the ballistic method of observation has been employed, the arrangements of which have been already described§. The nickel wire used contains nearly 98 per cent. of nickel and only 0.7 per cent. of iron; the iron wire is also, judging from its small specific resistance, nearly pure. The mode of conducting the experiments may be illustrated by the aid of fig. 1; this figure refers to a piece of well-

* Communicated by the Physical Society: read March 21, 1890.

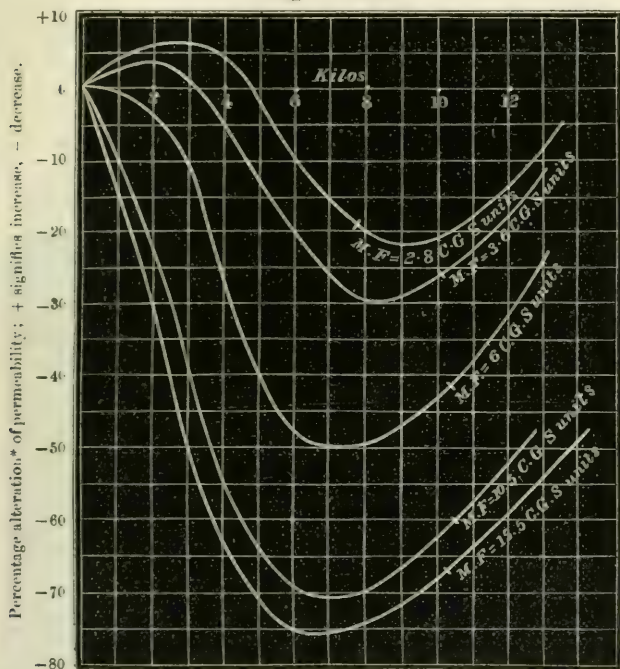
† The author begs to acknowledge with thanks the assistance which he has received in this investigation from the Elizabeth Thompson Science Fund, U.S.A.

‡ The magnetization which disappears on the removal of the magnetizing force.

§ Phil. Mag. xxv. p. 372.

annealed iron wire 1 millim. in diameter. The wire was in the first instance loaded with 12 kilos (the highest load employed in the experiment), and was subjected to a magnetizing force of 15.5 C.G.S. units which was alternately applied (always in the same direction) and removed until the deflexions of the ballistic galvanometer became constant. The load was then entirely removed, and the same force was again applied and removed as before. A load of 2 kilos was now put on the wire,

Fig. 1.—Iron.



and the same operations were repeated with this and the subsequent loads up to 12 kilos. Next the load was again entirely removed, and a similar series of observations was made with a magnetizing force of 10.5 C.G.S. units, and so on until the force had diminished to 2.8. The entire set of experiments was then repeated with ascending forces up to 15.5; this set did not sensibly differ from the one taken with descending magnetizing forces. As might be expected, each change of load produced

* If P_0 and P_n represent respectively the permeability with no load and a load of n kilos, the percentage alteration of permeability is taken to be $\frac{100(P_0 - P_n)}{P_0}$ or $\frac{100(P_n - P_0)}{P_0}$ according as the permeability is decreased or increased by loading.

an alteration in the *residual* magnetization, but this alteration does not concern us, and only the *temporary* changes, *i.e.* those which take place after repeated application of the force and when the deflexion on closing the battery-circuit is equal to that on opening it, are recorded in the figure.

It may be noticed that the Villari critical point depends upon the load, the greater the load the smaller the critical value of the force. This fact has been already observed by Sir William Thomson, but for a given load the Villari critical point is *much lower* when only the *temporary* magnetization is taken into account than when, as in Sir W. Thomson's experiments, the *whole* magnetization is observed. It occurred therefore to the author that though it might not be possible to reach the critical force for nickel as far as the total magnetization is concerned, such a value could nevertheless be found for *temporary* magnetization, and this has proved to be the case.

Fig. 2.—Nickel.

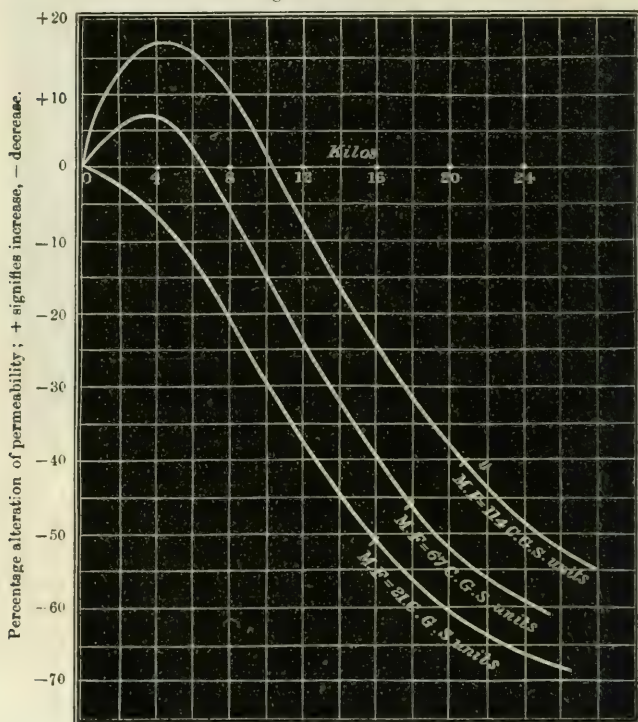


Fig. 2 refers to a nickel wire of .8 millim. diameter, which shows Villari critical points quite as striking as those of iron, but with this difference, that the critical value is *greater the*

greater the load, and for a given load is much greater in nickel than in iron.

With iron wire the curves may, and do, sometimes cut the load line *twice*, so that for a given value of magnetizing force there may be *two* loads which have no effect on the temporary magnetization. In fig. 1 none of the curves *actually* cut the load-line a second time, because the loading was not carried quite far enough; but with subsequent experiments made with the same wire and with the same loads at a temperature of 200° C. the two points of cutting were easily obtained, whilst the next figure shows that with greater loads the second point can be reached at the ordinary temperature of the room.

Fig. 3.—Iron*.

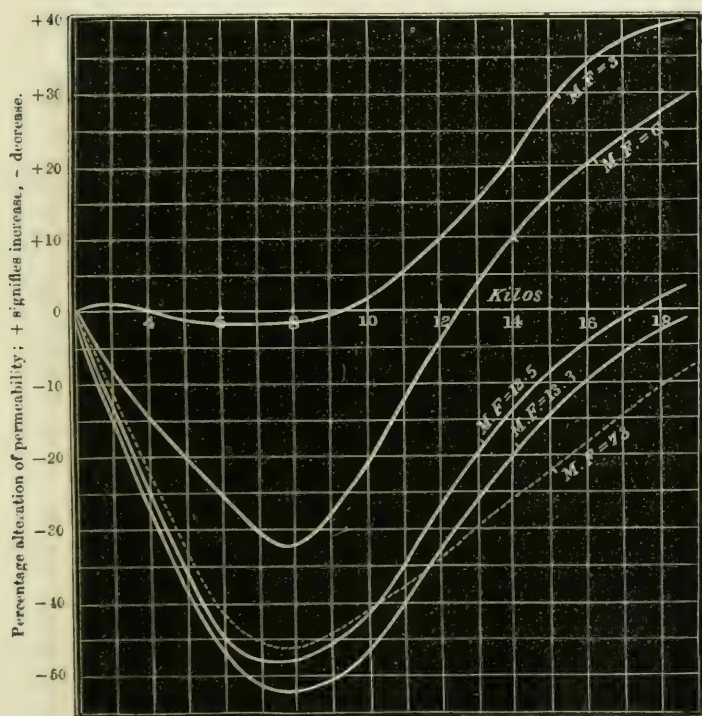


Fig. 3 illustrates the effect of loading on an iron wire of .077 millim. diameter, which in the first instance was

* In this experiment a load of 2 kilos was left permanently on the wire, so that the initial load is 2 instead of 0.

well annealed, but was subsequently loaded to very nearly its breaking-point, and was in consequence permanently lengthened by about 10 per cent., whereas the wire referred to in fig. 1 was not loaded sufficiently to produce any sensible permanent extension. For a magnetizing force of 3 C.G.S. units the curve cuts the load-line twice, but for higher forces the first cutting-point disappears and we have only the second one.

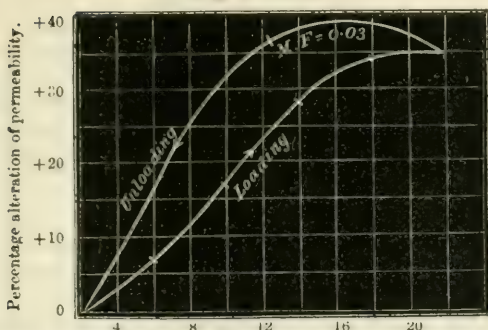
The maximum decrease of permeability is greater the greater the magnetizing force up to a certain limit of the latter, which limit other experiments (not illustrated by the figure) proved to be about 16 C.G.S. units. Beyond this limit the maximum decrease begins to become slowly less, as is shown by the dotted curve of the figure for which the magnetizing force was 73.

The curves for nickel can never be made to cut the load-line twice, for the wire of fig. 2 was stretched within one or two per cent. of its breaking-point, suffering thereby a permanent elongation of about five per cent. of its original length. The curves, however, show a *maximum* decrease of permeability with a load of about 24 kilos.

The observations hitherto recorded were only made at the different stages of *loading*, but subsequent ones showed that with nickel the readings on *unloading* were very nearly the same as those on *loading*, there being very little lagging of mechanical strain behind stress. Prof. Ewing has pointed out also that nickel exhibits very little *magnetic* hysteresis. With iron there is a very sensible lagging of mechanical strain behind stress, but the only effect of taking a mean between the observed changes on loading and unloading would have been to make the curves more parabolic in shape and not to alter their main character.

For the next two figures observations were made both on loading and unloading, and though the magnetizing force employed was here very minute, the curves show pretty nearly the same amount of lagging of mechanical strain behind stress which is experienced when much higher forces are used. For these very minute forces, of course, the apparatus had to be made much more sensitive, and the number of turns in the secondary coils was very great. Fig. 4 refers to the same kind of wire as that used in the first experiment. The wire in this case was, however, previously loaded to nearly its breaking-point. If the mean be taken of the percentage alterations of permeability on loading and unloading, the curve becomes exactly parabolic, with its axis vertical and its vertex at the point where the vertical from

Fig. 4.—Iron.

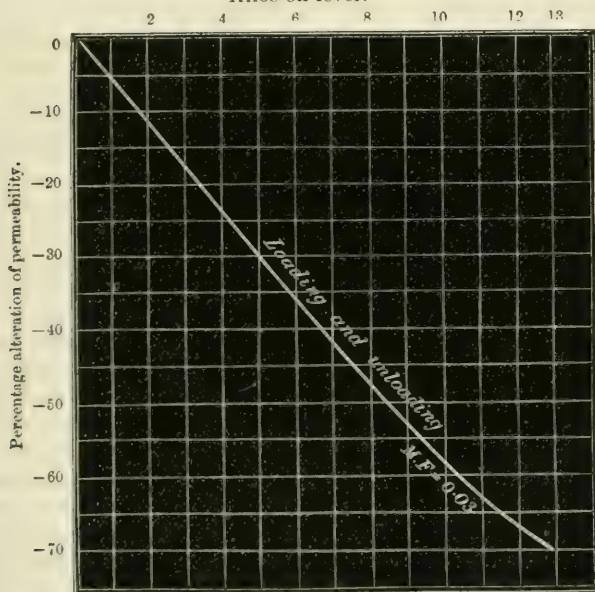


the load 16 kilos. cuts the curve. Both the loading and unloading curves lie entirely *above* the load-line, and there is no point of cutting this line.

Fig. 5 deals with a nickel wire of the same degree of purity as the first but $1\frac{1}{2}$ millim. in diameter. The stress

Fig. 5.—Nickel.

Kilos on lever.



1 kilo on the lever represents a stress of 2.68 kilos per sq. millim.

was carried by the aid of a lever to very nearly the breaking-point of the wire. There is in this case no perceptible lagging of mechanical strain behind stress, the curve on loading being

identical with that on unloading. With nickel the curve lies entirely *below* the load-line and never cuts the line.

In figures 4 and 5 the curves are described as having been obtained with a magnetizing force of 0.03 C.G.S. units ; but other experiments showed almost precisely the same curves to be obtained for any force between 0.03 and 0.3 C.G.S. units. Between these limits of force the *whole* of the magnetization is practically *temporary* provided the wires have been stretched to the extent these were.

From what has been said and from the figures it is easy to see what would be the general character of the curves, showing the relation between change of temporary permeability and change of load for any magnetizing force whatever. If a piece of iron wire be tested with loads nearly up to the breaking-point, then for magnetizing forces ranging from 0 to somewhere about .3 C.G.S. units the curves will be *identical* with those of fig. 4, and will not cut the load-line. For a value of force above .3 the curves will cease to be identical, the maximum increase of permeability will become less and less as the force increases until for a certain force the curve begins to cut the load-line. As the force increases beyond this value the point of cutting approaches nearer and nearer to the origin of coordinates, and the curve begins eventually to cut the load-line in two points. The first point of cutting, as the force increases still further, gets nearer and nearer to the origin, whilst the second point gets further and further away from it ; and when the magnetizing force reaches a value but little over 3 C.G.S. units, the first point vanishes and the second point only remains. Finally, with a sufficiently high force it would seem that the second point also cannot be reached and the curve now lies *entirely beneath* the load-line, whereas for very minute forces it lies *entirely above* this line.

With nickel the curves for very minute magnetizing forces are, like those of iron, exactly the same for different values of the force, but instead of lying *above* the load-line lie *entirely below* it. Beyond a certain limit of the force the curves cease to be identical and the maximum decrease of permeability begins to become less and the curve near its origin to bulge more and more towards the load-line, until for a value of force a little over 21 C.G.S. units the permeability begins to increase with small loads and to cut the load-line in one point, which gets shifted further and further away from the origin as the force increases.

XLIV. *On a New Method and Department of Chemical Research.* By Dr. G. GORE, F.R.S.*

CONTENTS.

METHOD OF WORKING	PAGE 401
-------------------------	-------------

CURVES OF ELECTROMOTIVE FORCE.

A. *By Varying the Strength of the Solution at Both Metals.*

	Strength of Solution. Substance.	Water.		PAGE
Curves of Chlorine, Bromine, and Iodine	·001 to ·01 grain in 155 grains.			403
" HCl, HBr, and HI. <i>Weak</i>	·001 to ·01 " "			405
" HNO ₃ , and H ₂ SO ₄ "	·001 to ·01 " "			406
" H ₂ SO ₄ at 60° C. "	·001 to ·01 " "			407
" HCl, HBr, and HI. <i>Strong</i>	·1 to 1 " "			409
" HCl with Cadmium as Positive Metal	·1 to 1 " "			409
" KCl, KBr, and KI	·1 to 1 " "			410
" KBr, at 60° C.	·1 to 1 " "			411
" NaCl, NaBr, and NaI	·1 to 1 " "			412
" KClO ₃ , KBrO ₃ , and KIO ₃	·7 to 1·7 " "			413
" K ₂ SO ₄ and Na ₂ SO ₄	·1 to 1 " "			414
" KCl + KI, and KCl + NaCl	·1 to 1 " "			415
" Isomeric Solutions	·01 to ·1 " "			416

B. *By Varying the Strength of the Solution at One Metal only.*

Curves of KBr, NaCl, and KCl.....	·1 grain in 465.		PAGE 417
-----------------------------------	------------------	--	-------------

C. *By Varying the Temperature of the Solution at Both Metals.*

Curve of HCl from 10° to 100° C.	·03 grain in 465.		PAGE 419
---------------------------------------	-------------------	--	-------------

D. *By Varying the Temperature of the Solution at One Metal only.*

Curve of Cold Zinc and Hot Platinum from 17° to 100° C.	39 grains in 465.		PAGE 420
" Cold Platinum and Hot Zinc from 15° to 100° C.	39 grains in 465.		420

E. *General and Theoretical Considerations.*

METHOD OF WORKING.

IN an investigation "On the Change of Potential of a Voltaic Couple by Variation of Strength of its Liquid" (Roy. Soc. Proc. 1888, xlv. p. 296), I showed that by immersing a small pair of unamalgamated zinc and platinum plates in distilled water, then adding to the water successive small and equal quantities of a particular halogen, acid, or salt, until a more or less saturated solution was formed, and measuring by the method of balance with a galvanometer in the circuit, with a suitable thermoelectric pile (see Proc. Birm. Phil. Soc. iv. p. 130; also 'The Electrician,' 1884, xii. p. 414), aided when necessary by a zinc-platinum distilled water-cell, or a Clark's standard cell, the degrees of electromotive force produced by each addition of substance, the changes of that force did not vary by a regular gradation. And I stated that

* Communicated by the Author.

"by plotting the quantities of dissolved substance as ordinates to the degrees of electromotive force as abscissæ, each substance or mixture of substances yielded a different curve of electromotive force on uniformly changing the degree of strength of its solution." And that "with a given voltaic couple at a given temperature, the curve was constant and characteristic of the substance." The examples given in this paper illustrate these statements, and the measurements were made by the above method.

Instead of employing a thermopile, the following plan with the "voltaic balance" might be adopted:—1st. Balance two small zinc-platinum voltaic cells with distilled water in each, and a galvanometer of 100 ohms resistance in the circuit, then add gradually sufficient of the exciting substance to one of the cells to just visibly upset the balance, and note the quantity added. 2nd. Balance the cells with a very weak solution containing one unit quantity of the substance in each cell; then add a sufficient excess of the substance to one cell to again upset the balance, and note the amount of excess. 3rd. Balance the cells with a two unit quantity solution, and upset the balance again in like manner. And so on through such a series of strengths of solution as may be desired to obtain a curve. The proportions of excess of substance added to the amount of water in the cell represent the relative amounts of voltaic energy of the different strengths of liquid.

This method is very much more sensitive than the one with the thermopile, for whilst the latter only divides the range of difference of potential between water and chlorine for example ($=.753$ volt), in practical working into about 15,000 parts, the former divides it into 1200 millions. On the other hand, whilst by the thermopile method the values of the unit of measurement are equal throughout a series, those of the numbers obtained by the voltaic-balance one vary with the degree of strength of the solution. The following instance illustrates this:—

The liquid employed was a solution of potassium sulphate, and the balancing couples were formed of zinc and platinum. The table shows the degrees of strength of the solution, and the proportions of additional salt required with each to upset the balance.

Strength of Solution.		Excess of K_2SO_4 .	
K_2SO_4 .	Water.	K_2SO_4 .	Water.
1.0 grain	155 grains.	.30 grain	= 1 in 51.6
.5 "	" "	.25 "	= 1 in 60.0
.1 "	" "	.20 "	= 1 in 77.5

The degree of sensitiveness of the balance therefore increased directly as the degree of dilution of the solution.

A. CURVES OBTAINED BY VARYING THE STRENGTH OF THE SOLUTION AT BOTH METALS.

Nearly all the measurements of electromotive force given in this paper were made with highly pure substances, and in section "A," with the exception of one instance only (see fig. 8), each curve starts from the potential of unamalgamated zinc and platinum in distilled water at about $16^{\circ}\text{C.} = 1.127$ volt. The quantity of distilled water employed as the solvent was in nearly every case 155 grains, and the series of degrees of strength of the solutions of each substance were usually such as could best be worked by the process, *i. e.* neither too strong nor too weak, and were with different substances either the same or so arranged as to best enable comparisons to be made between the results of the different series of measurements; they were not always sufficiently strong to fully develop the most characteristic curves.

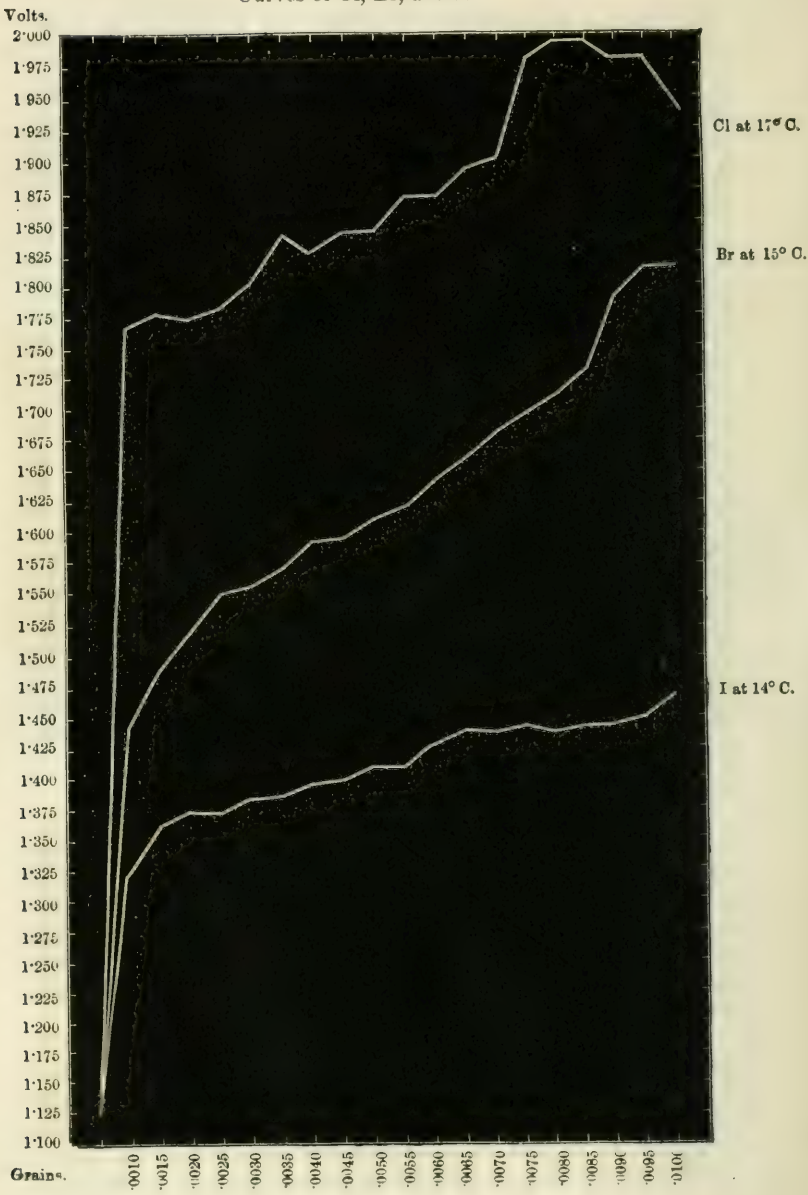
For each separate measurement, with the solutions of the halogens and the strong ones of the acids, a fresh portion of the original liquid was taken; with those of other substances the zinc was so feebly acted upon and the liquid so slightly altered in composition, that this was not found necessary. With solutions of salts, the presence of films of oxide upon the zinc was tested for by replacing the saline liquid by distilled water, and then observing whether the cell was still exactly balanced by a zinc-platinum water one. No trouble was experienced from polarization caused by hydrogen in the platinum plates, nor by atmospheric air dissolved in the water.

1. *Curves of Chlorine, Bromine, and Iodine.*

The range of strength of the solutions of each substance was from .001 to .01 grain in 155 grains of water. With solutions of these substances the degree of electromotive force increased somewhat with the period of immersion; this difficulty was due to the great chemical energy of the substances, and was overcome by making the fluctuations of the galvanometer-needles equal on each side of zero.

These curves show:—1st. An increase generally of electromotive force attending increased strength of solution. 2nd. A much greater increase caused by the first amount of substance added than by the subsequent additions. 3rd. A gradation of degree, both of first increase and of maximum electromotive force in the three curves, varying inversely as

Fig. 1.
Curves of Cl, Br, and I.



the magnitudes of the atomic weights of the substances. 4th. A general similarity of form, sufficient to show a graduated degree of likeness. And 5th. A sufficient degree of difference of form to characterize each individual substance.

2. Curves of HCl, HBr, and HI.

a. *Weak Solutions.*

Each acid was pure and colourless. The solutions were of the same range of degrees of strength as those of the halogens, in order to compare the effects of the two groups of substances; and the curves are all drawn on the scale of magnitude in each direction as those of the halogens.

Fig. 2.

Curve of HCl at 10° C.—*Weak Solution.*

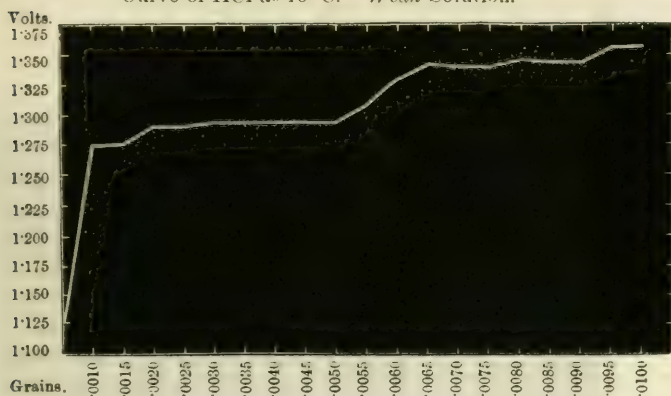
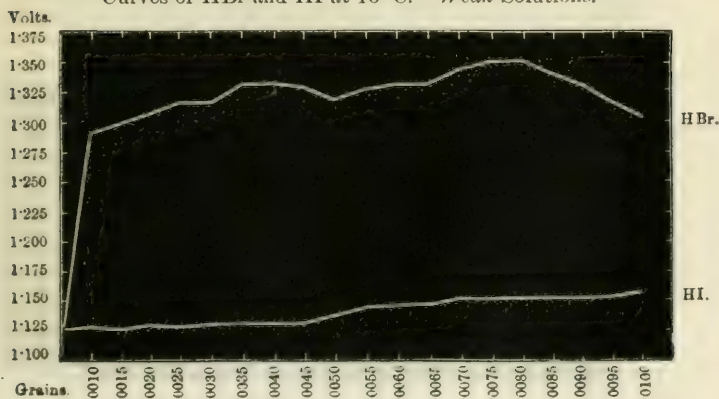


Fig. 3.

Curves of HBr and HI at 16° C.—*Weak Solutions.*



The curves show :—1st. That the union of hydrogen with the halogens greatly diminished the electromotive force. 2nd. A feeble increase of electromotive force, greatest at the commencement, especially with hydrochloric and hydrobromic acids, attending increased strength of the solution. 3rd. A less degree of family likeness than in the curves of the halogens. 4th. The substance of largest molecular weight gave the smallest increase of electromotive force. And 5th. Each substance gave a characteristic curve. The general feebleness of character of the curves was due to the weakness of the solutions (compare fig. 7, of curves of solutions 100 times stronger).

3. Curves of HNO_3 and H_2SO_4 .

The acids were pure and the range of degrees of strength of their solutions was the same as those of the weak ones of hydrochloric, hydrobromic, and hydriodic acids.

Fig. 4.

Volts. Curve of HNO_3 at 14°C .—*Weak* Solution.

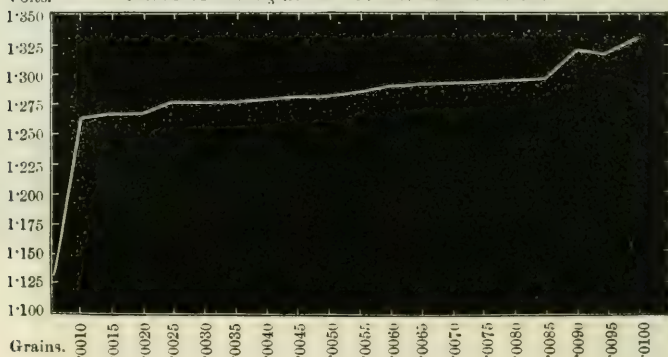
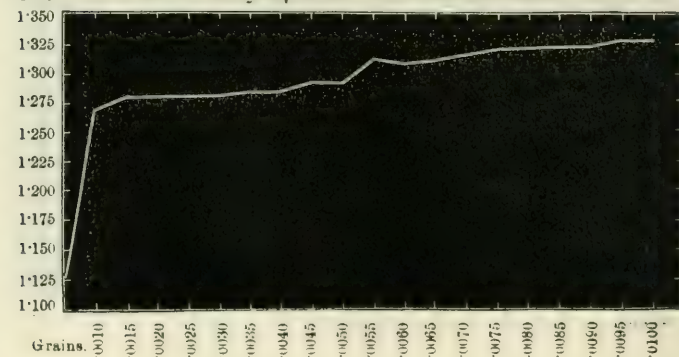


Fig. 5.

Volts. Curve of H_2SO_4 at 15°C .—*Weak* Solution.



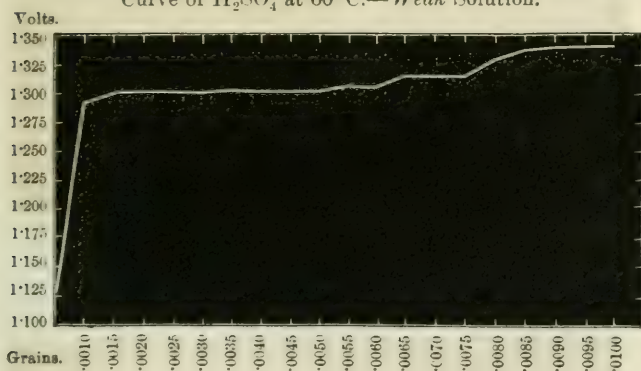
The curves are drawn upon the same scale as those of the weak solutions of the above-named acids. 1st. They are very greatly different from those of the halogens, and show very much smaller degrees of electromotive force. 2nd. Their differences from those of hydrochloric, hydrobromic, and hydriodic acid of the same range of degrees of strength are also quite conspicuous. And 3rd. They are sufficiently unlike to be characteristic of each substance and to be clearly distinguishable from each other. The solutions employed were too weak to fully show the characteristic forms of the curves; the degrees of strength were chosen chiefly to enable the curves to be compared with those yielded by the halogens and by their acids.

4. Curve of H_2SO_4 at 60°C .

The range of degrees of strength of the solution was the same as in the previous case, viz. from .001 to .01 grain of the substance in 155 grains of water.

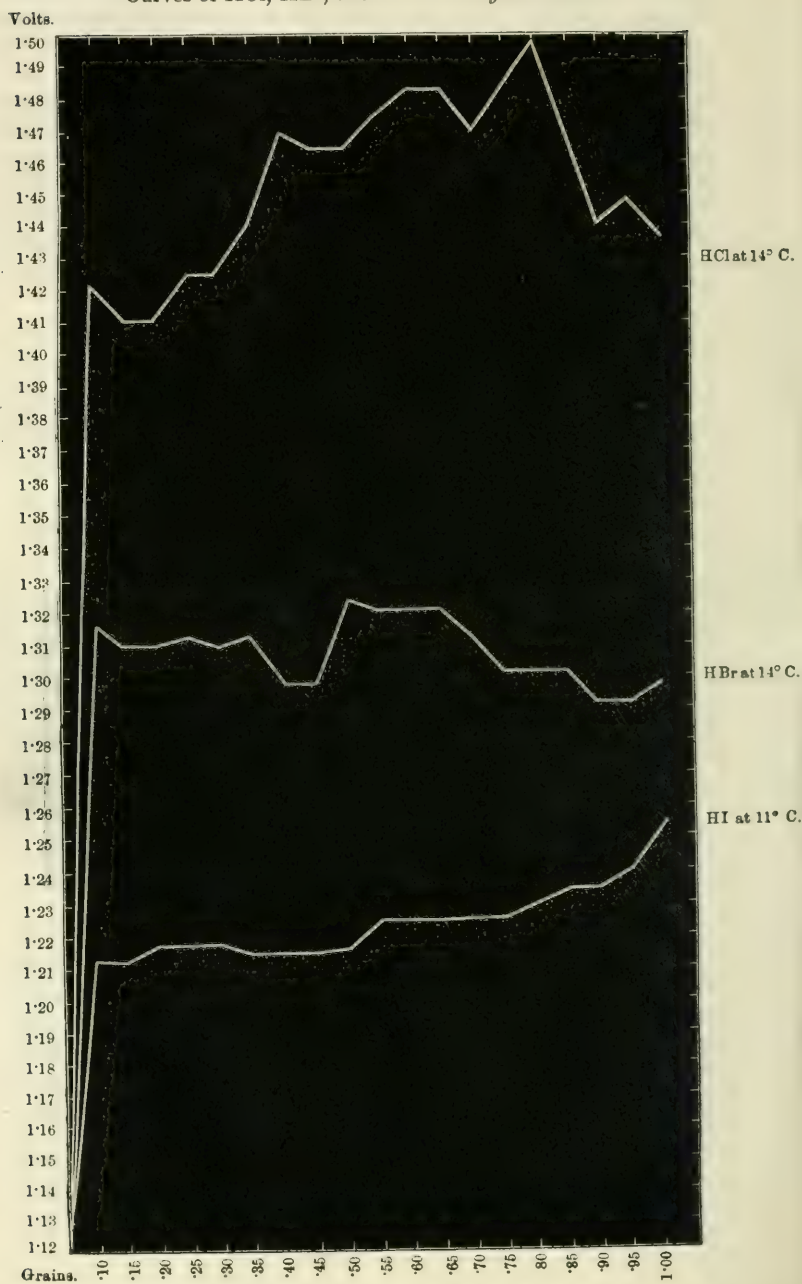
Fig. 6.

Curve of H_2SO_4 at 60°C .—*Weak Solution*.



By comparing the curves obtained at the two different temperatures, we find that a rise of temperature caused a general increase of electromotive force, greatest at the commencement, and quite sufficient to distinguish the one curve from the other. The difference would probably be much greater with stronger solutions (compare figs. 9 and 10 of KBr at 18°C . and 60°C .).

Fig. 7.

Curves of HCl, HBr, and HI.—*Strong Solutions.*

5. *Curves of HCl, HBr, and HI.*b. *Strong Solutions.*

These solutions were one hundred times stronger than the previous ones in order to fit them for comparison with those of the corresponding salts; they contained from .10 to 1.0 grain of substance in 155 grains of water. The degrees of electromotive force of the solution of hydrochloric acid were variable, and those of the other two acids less so.

These curves are drawn upon a scale 2.92 times as large vertically as those of the previous ones, in order to fit them for comparison with those of the corresponding salts. They show:—1st. A general increase of electromotive force attending gradually increased strength of liquid. 2nd. A much larger increase produced by the first amount of substance added than by the succeeding ones. 3rd. A gradation of degree of general increase of such force varying inversely as the magnitudes of the molecular weights of the substances. And 4th. A great dissimilarity of form characteristic of each individual substance.

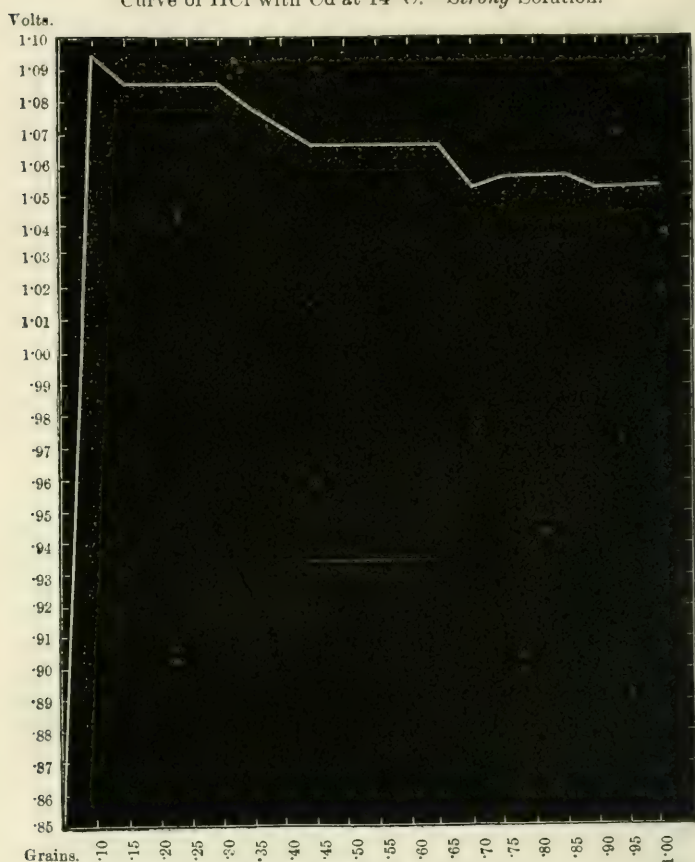
By comparison with the curves yielded by the weak solutions of the three acids, those of the strong ones show:—1st. A much greater increase of electromotive force, both on the addition of the first amount of the substance and by the subsequent additions. 2nd. A more distinct relation of those increases to the magnitudes of the molecular weights of the substances. 3rd. Much more characteristic curves. And 4th. A much greater degree of irregularity of form of curve; this greater irregularity of form was a genuine effect, and was not due to temporary fluctuations of the current.

6. *Curves of HCl with Cadmium as Positive Metal.*

The range of degrees of strength of the solutions in this case was the same as that of the "strong" solution of the same acid in the immediately previous group of acids, and the scale of magnitude upon which the curve is drawn is the same. The electromotive force was variable, owing to the strength of the solutions, and of course started from a lower point than when zinc was used as the positive metal.

On comparing the curve with the one yielded by zinc in the same degrees of strength of solution of the same acid, we find:—1st. Quite a different form of curve. 2nd. A smaller increase of electromotive force on adding the first portion of acid. 3rd. A general decrease of that force by the further additions. And 4th. A curve characteristic of the substance.

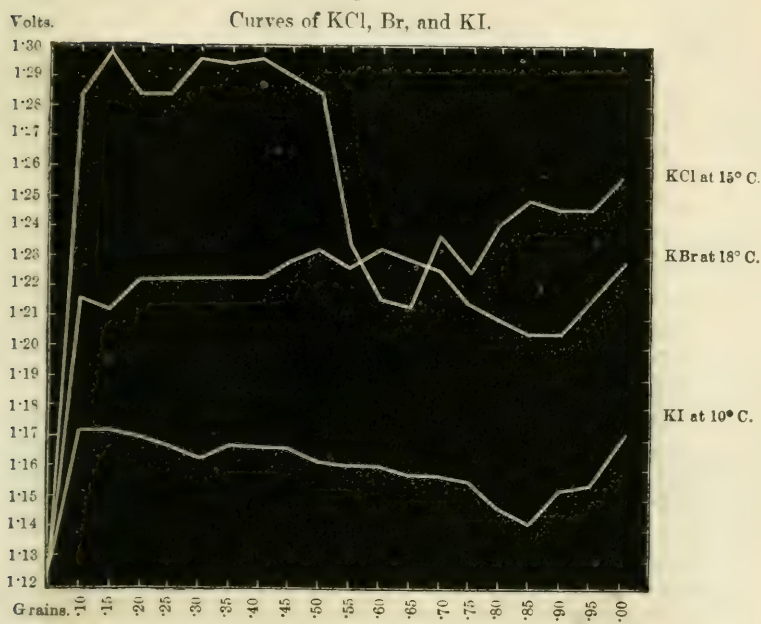
Fig. 8.

Curve of HCl with Cd at 14° C.—*Strong Solution.*

7. *Curves of KCl, KBr, and KI.*

All the substances were highly pure, colourless, and inodorous; the iodide was very faintly alkaline. The solutions were of the same range of degrees of strength as the strong ones of the corresponding acids, viz. from .1 to 1.0 grain of substance in 155 grains of water. The electromotive force of the zinc-platinum couple increased somewhat with the period of immersion. The absence of solid films upon the zinc was proved by occasionally replacing the saline liquid by distilled water, and observing whether the cell was still exactly balanced by a zinc-platinum water one.

Fig. 9.



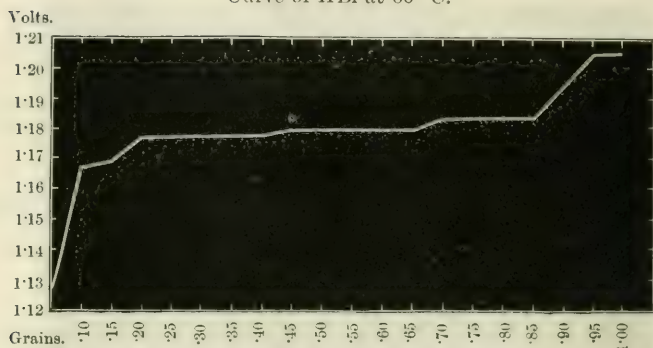
The curves of these substances are all drawn upon the same scale of magnitude as those of the "strong" solutions of the corresponding acids. They show:—1st. A much greater increase of the electromotive force caused by the first amount of substance added than by the subsequent ones. 2nd. A gradation of degree of first increase and of maximum electromotive force, varying inversely as the magnitudes of molecular weight of the substances. 3rd. Large differences of form, characteristic of each individual substance. And 4th. The substitution of potassium for hydrogen in the corresponding acids lowered the electromotive force in all three cases, and the amount of this reduction varied inversely as the magnitudes of the molecular weights of the substances; the union of potassium with the halogens had similar effects, but in much greater degrees (compare the respective figures).

8. Curve of KBr at 60° C.

The range of degrees of strength of the solution in this case was the same as in the previous one when the liquid was at 18° C., and was from .10 to 1.0 grains of substance in 155 grains of water.

Fig. 10.

Curve of KBr at 60° C.



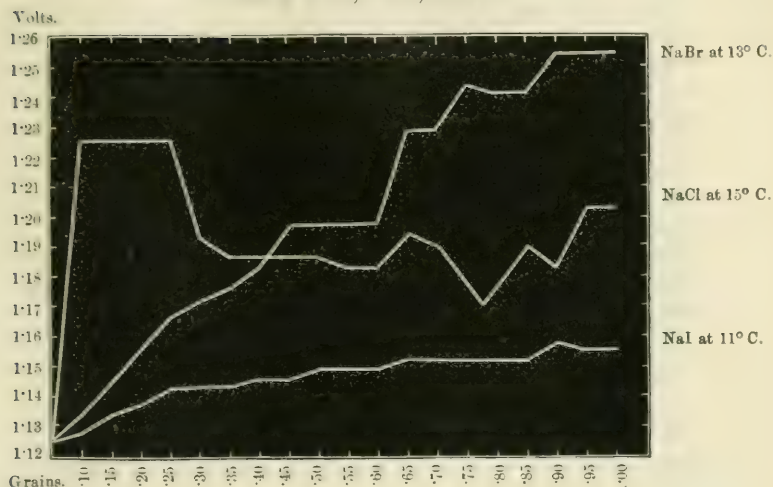
On comparing the two curves obtained at the two temperatures we find considerable differences, viz.:—1st. A great unlikeness of general form. 2nd. A general and large diminution of electromotive force at the higher temperature. And 3rd. A much smaller increase of that force on the addition of the first portion of the substance. The differences would probably have been less conspicuous if the solutions in each case had been much weaker. These results support the conclusion that potassium bromide behaves to a certain extent like a different substance at each different temperature.

9. Curves of NaCl, NaBr, and NaI.

The chloride contained a trace of sulphate, and the bromide and iodide were very faintly alkaline. The solutions were of the same range of degrees of strength as the corresponding salts of potassium; and the curves are drawn upon the same scale of magnitude.

These curves show:—1st. A general increase of electromotive force by increase of dissolved substance. 2nd. A great difference of form, and strongly characteristic curve in each case. And 3rd. The substitution of sodium for potassium in each salt considerably reduced the degree of electromotive force produced by the first addition of the substance, and the amount of this reduction varied inversely as the molecular weights of the salts. The curves are widely different in form from those of the corresponding salts of potassium, and this is no doubt entirely due to the difference of metallic base; in each group, however, the curve of the chloride intersects that of the bromide.

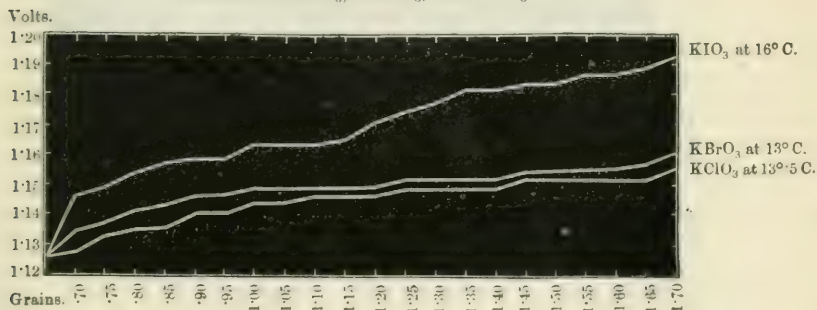
Fig. 11.
Curves of NaCl, NaBr, and NaI.



10. Curves of KClO_3 , KBrO_3 , and KIO_3 .

The chlorate contained a trace of chloride. In consequence of the degrees of electromotive force produced by solutions of these salts being so little greater than that produced by water alone, viz. 1.127 volt, it was necessary to use much stronger solutions than those of the previous substances; the ones employed contained from .7 to 1.7 grains in 155 grains of water.

Fig. 12.
Curves of KClO_3 , KBrO_3 , and KIO_3 .



The curves show:—1st. A striking similarity of general form, very different from that of the corresponding chloride, bromide, and iodide; this was probably chiefly due to the general feebleness of the action. 2nd. A very small increase of electromotive force in each case on adding the first portion of substance, and on subsequent additions; and the amounts of these increases, contrary to what happened with other groups of substances, varied *directly* as the magnitudes of the molecular weights of the salts, but the degree of reversed action was not conspicuous. 3rd. A sufficient difference of form to characterize each substance. And 4th. The chemical union of oxygen with the three corresponding halogen salts, reduced the general electromotive force in each case, and the amount of reduction varied inversely as the magnitudes of the molecular weights of the salts (compare fig. 9).

11. Curves of K_2SO_4 and Na_2SO_4 .

The potassium salt was very pure; the sodium one contained traces of chloride. The solutions were of the same range of degrees of strength as those of the halogen salts of the same metals, viz. from .1 to 1.0 grain of salt in 155 grains of water.

Fig. 13.

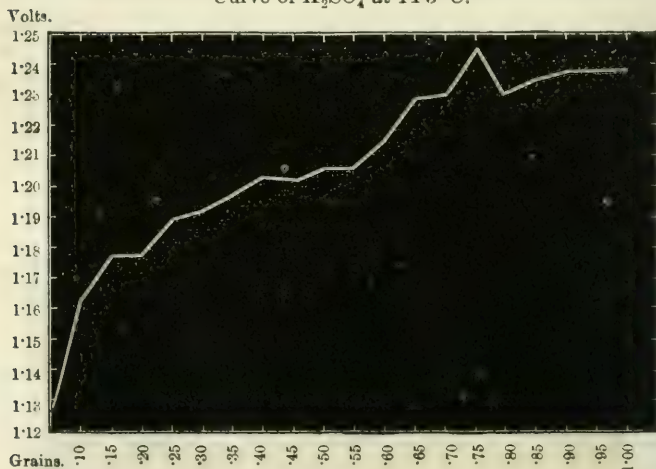
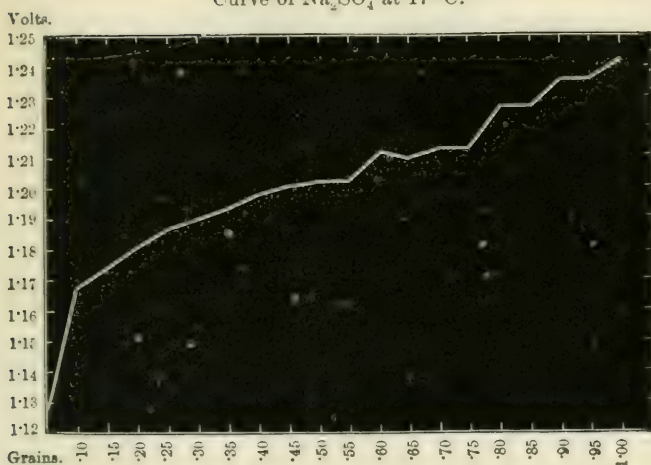
Curve of K_2SO_4 at $14.5^\circ C$.

Fig. 14.

Curve of Na_2SO_4 at 17°C .

These two curves are largely alike, due to their being those of closely allied salts of the same acid ; but somewhat different in consequence of difference of their metallic bases. They are both considerably different from those of the chlorides, bromides, and iodides of the same metals.

12. Curves of $\text{KCl} + \text{KI}$, and $\text{KCl} + \text{NaCl}$.

The measurements of electromotive force of these were made to ascertain the influence of more complex compounds upon the amount of that force. The salts were mixed in the proportions of their molecular weights, and the proportions of mixtures taken were the same as those of the same salts separately in previous experiments, viz. from .1 to 1.0 grain in 155 grains of water.

Fig. 15.

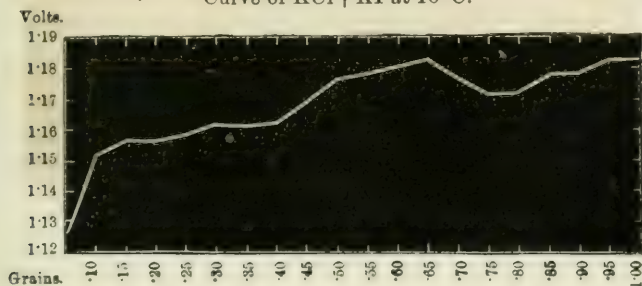
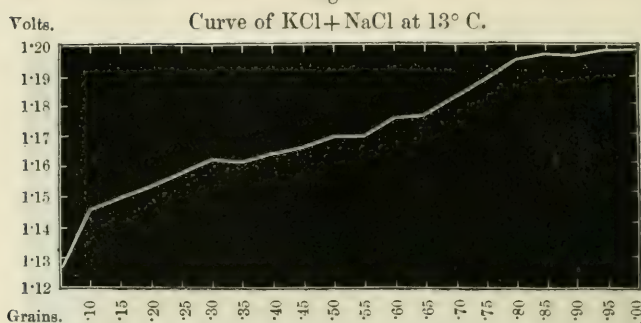
Curve of $\text{KCl} + \text{KI}$ at 16°C .

Fig. 16.



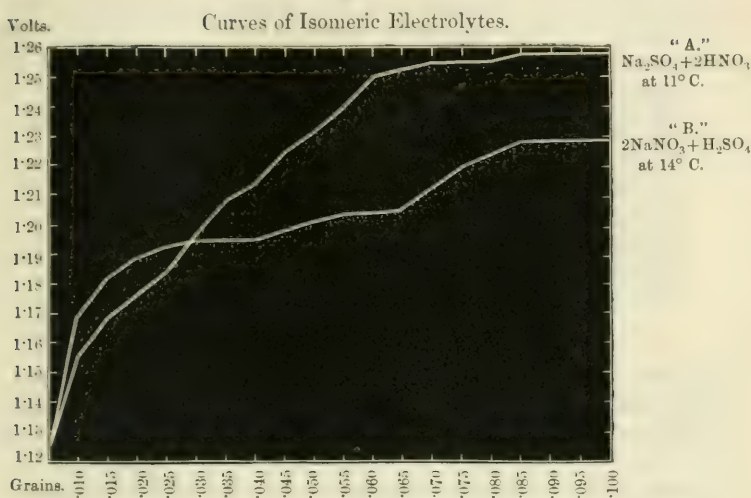
1st. Each of the curves is strikingly unlike in general form each of those of the constituent salts of the compound, and the form is not in either case an average of that of the two; each of them also shows a great reduction of electromotive force due to the chemical union of the two constituents. 2nd. In each case an increase of strength of solution is attended by an increase of electromotive force. 3rd. The two curves are each characteristic of the individual substances.

The amounts of voltaic energy of the dissolved salts separately before chemical union were :—KCl=699,803, NaCl=207,589, and KI=16,361; and after the union those of the compounds were :—KCl+KI=7,571, and KCl+NaCl=5,959 (see “Relative Amounts of Available Voltaic Energy of Aqueous Solutions,” *Proc. Birm. Phil. Soc.* vii. part i.).

13. *Curves of Isomeric Electrolytes.*

I have already shown (see *Phil. Mag.* October 1889, p. 289, “On the Molecular Constitution of Isomeric Solutions”) that aqueous isomeric electrolytes yield different amounts of voltaic energy with a zinc-platinum couple. In the present case I employed the same pair of mixed aqueous solutions as were used in that research, viz. an unstable one “A” having a composition represented by the formula $\text{Na}_2\text{SO}_4 + 2\text{HNO}_3$, and yielding an average voltaic energy = 77,446; and its stable isomer “B” represented by $2\text{NaNO}_3 + \text{H}_2\text{SO}_4$, and yielding 32,722. The degrees of strength of the series of solutions employed were those which were the most easily worked, and were from .01 to .1 grain of the mixture in 155 grains of water. The constituent solutions of “A,” previous to being mixed, contained .01 grain of substance per cubic centimetre; if they were stronger than this there was risk of the liquid undergoing a chemical change during the mixing.

Fig. 17.



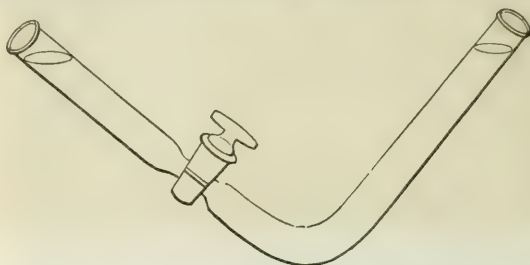
These curves show much more completely than any single pair of measurements of voltaic energy could do, the considerable differences between the molecular and chemical constitutions of the two liquids. Nearly throughout its entire range the curve of "A" shows a greater degree of electromotive force than that of "B."

As the unstable liquid "A" is readily changed into the stable one "B" by merely heating it to nearly 100°C . in a stoppered glass flask during fifteen minutes, and then would give the curve of "B," it is evident that the method of examining aqueous solutions by means of curves of electromotive force is applicable for detecting and measuring chemical and molecular changes in them.

B. CURVES BY VARYING THE STRENGTH OF THE SOLUTION AT ONE METAL ONLY.

The kind of apparatus employed is shown by the annexed sketch, and is formed of glass. A weak solution, containing 1 grain of the substance in 465 grains of water, was put, together with the negative metal, platinum, into the short leg of the tube, and successive portions of solution, of regularly decreasing strength, in 465 grains of water, were put, together with the positive metal, unamalgamated zinc, into the long leg, and the electromotive force with each strength of solution was measured. The positions of the metals were then reversed, and the measurements repeated. The glass

tap was closed during the process of changing each strength of liquid. In consequence of the much greater conduction resistance in the constricted portions of the solutions, the degrees of electromotive force were all much smaller than if



the two metals had been near each other in the same leg. The following are the results obtained with solutions of KBr and NaCl :—

Fig. 18.

Curve of KBr, by Varying Strength of Solution at One Metal only, at 16°·5 C.

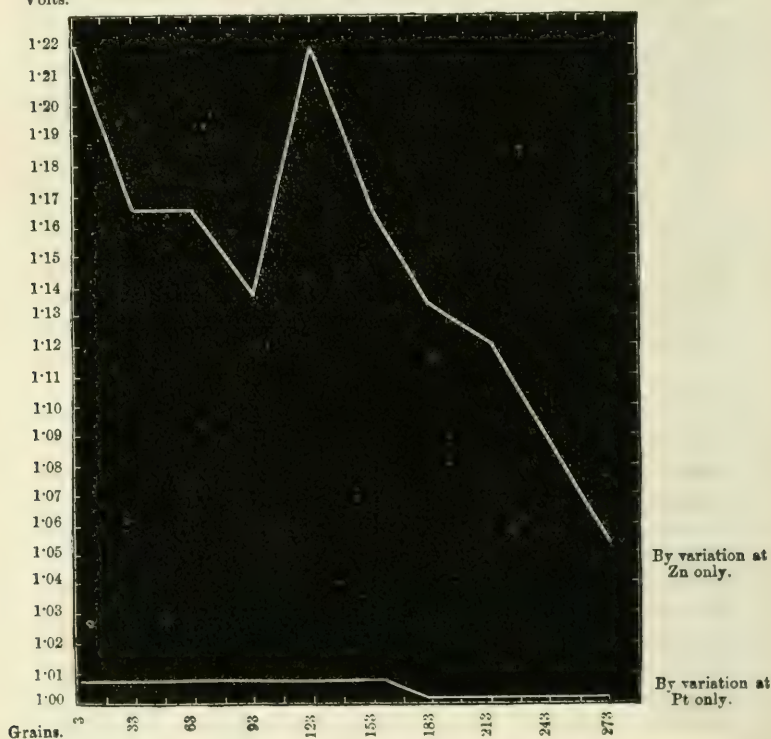
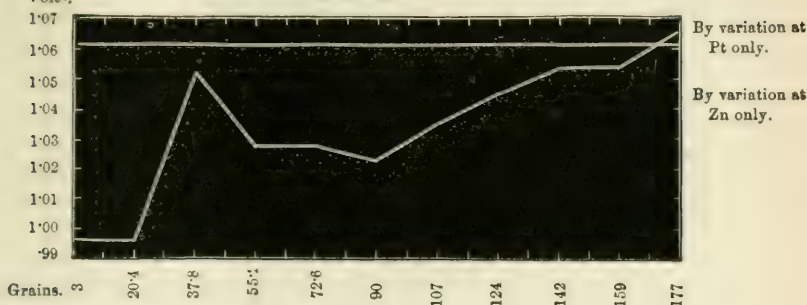


Fig. 19.

Curve of NaCl, by Varying Strength of Solution at One Metal only,
at 15° C.



The curves show that the variation of strength of the liquid had a large effect upon the electromotive force at the surface of the zinc, but scarcely any such effect at that of the platinum; and we may conclude that when such variation of strength occurs at both metals simultaneously, the effect upon the electromotive force, and consequently also upon the form of the curves, is nearly wholly due to changes of chemical action at the surface of the zinc, and but little to such changes at the platinum.

In a third similar experiment, with a solution of 1 part of potassium chloride and 465 parts of water at 15°·5 C. in the short leg, and one of the same salt, varying in strength equally in nine successive portions from 3 to 147 grains, in 465 grains of water in the long leg, the changes of strength had no perceptible influence upon the electromotive force, which remained constant at 1.1544 volts whichever metal was in the longest leg.

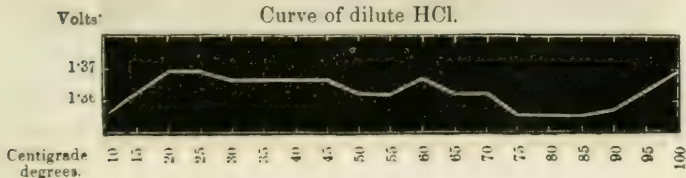
C. CURVES BY VARYING THE TEMPERATURE OF THE SOLUTION AT BOTH METALS.

Curve of Dilute HCl.

The solution contained .01 grain of HCl in 155 grains of water, and the electromotive force was measured every five Centigrade degrees from 10° C. to 100° C.

Fig. 20.

Curve of dilute HCl.



This curve shows :—1st. That the electromotive force varies with the temperature. And 2nd. That a regular variation of temperature of the solution is attended by an irregular change of electromotive force. It is probable that the curve obtained by varying the temperature is characteristic of the substance, and would be different with every different substance and degree of strength of its solution.

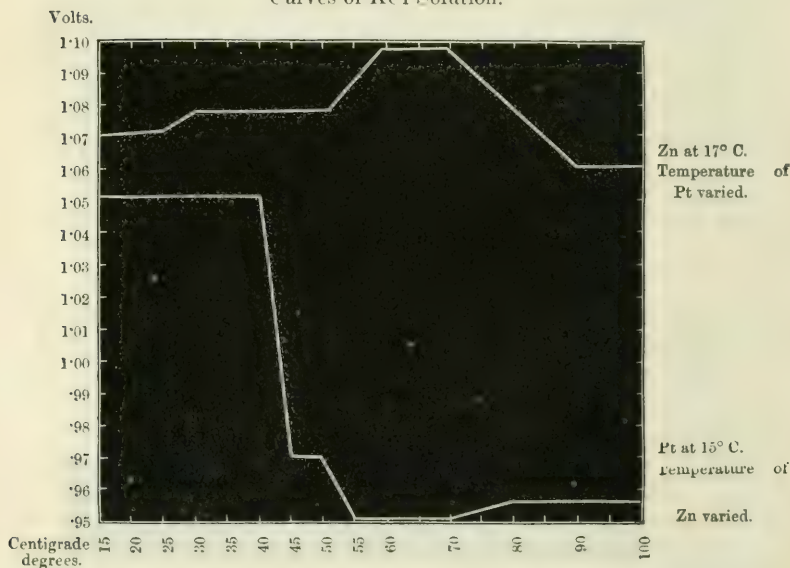
In a similar experiment with a solution of .027 grain of chloride of ammonium in 465 grains of water, the electromotive force of the zinc-platinum couple remained constant at .9084 volt at all temperatures between 14° and 100° C., and then very slightly increased.

D. CURVE BY VARYING THE TEMPERATURE OF THE SOLUTION AT ONE METAL ONLY.

In these measurements the large bent glass tube was employed (see section "B"). The liquid consisted of 39 grains of potassium chloride dissolved in 465 grains of previously boiled distilled water. In one series of measurements the zinc was immersed in the heated portion of liquid and the platinum in the cold portion; and in the other series the reverse. The following are the curves obtained :—

Fig. 21.

Curves of KCl Solution.



The two curves are very different. The greatest variation of electromotive force was at the zinc, and was = $\cdot 103$ volt, whilst that at the surface of the platinum was only = $\cdot 04$ volt.

The results show that the change of electromotive force which occurred on gradually heating an electrolyte and the two metals in it is a concrete effect of two influences, one of which is situated at the surface of the positive metal and the other at that of the negative one. Each of these two influences itself would also probably be a compound effect of the separate actions of heat upon the metal and upon the liquid.

These general effects of variation of temperature described in sections "C" and "D" are very similar to those of change of strength of liquid given in sections "A" and "B."

E. GENERAL AND THEORETICAL CONSIDERATIONS.

The evidence obtained by this research shows:—1st. That every different electrolytic substance when in aqueous solution gives, by varying the degree of strength of its solution (or by varying its temperature), a different curve of electromotive force. 2nd. That this curve is characteristic of the substance. 3rd. That under these conditions, substances which constitute a recognized chemical group yield a series of curves which usually exhibit a gradation of likeness of form. 4th. That the degrees of electromotive force of such a group usually vary in magnitude inversely as the amounts of the atomic and molecular weights of the substances. 5th. That a much greater increase of electromotive force is usually caused by the first amount of substance added to the water than by the subsequent amounts. 6th. That the chemical union of two substances to form a soluble salt is attended by a definite decrease of electromotive force and a definite change of form of curve. 7th. That the substitution of one halogen, acid, or metallic base for another in the composition of a soluble electrolytic salt, is accompanied by a definite amount of change of that force and of the form of its curve; and it will be possible to trace, by means of these changes, the presence of each halogen, acid, and metal in the various solutions of its salts. 8th. That isomeric solutions of electrolytic substances give different curves under the same conditions, and may thus be distinguished from each other. 9th. That molecular and chemical changes and their rates, in electrolytes, may be examined and measured by this method. And 10th. That if the solutions of the substances are too weak, the characteristic forms and differences of the curves are not fully developed,

and if they are too strong the measurements of electromotive force are more difficult to make. As the measurements were made at the null point when no current was passing, the curves represent the electromotive forces and molecular motions which exist under that condition; when the current passes, the molecular movements are greatly altered.

The changes of electromotive force and forms of curve obtained,—1st, by the same variations of strength of the same solution at two different temperatures; 2nd, by varying the temperature of a solution without changing its strength; and 3rd, by varying its temperature at the positive metal only, or at the negative one only,—support the general view that each substance becomes more or less a different substance at each different temperature, and that the degrees of property of each substance at different temperatures are practically infinite in number.

The results in general support the kinetic theory that the most fundamental attribute of matter is motion, that a mass of matter is a mass of motion, that each substance consists essentially of a collection of molecular motions, and that the chief properties of bodies are consequences of such motions. Changes of volta-electromotive force are now generally recognized as being due to those motions, and as being disturbances of the universal æther which pervades all bodies and all space. Each degree of such force may also be regarded as a concrete result of an extensive series of molecular vibrations of extremely varied degrees of amplitude; this series being characteristic of the particular material combination producing it, analogous to the collection of vibrations producing a beam of light of a particular burning substance. The curves represent in addition the changes in amount of these motions; and by observing these changes in a single substance under a sufficient variety of conditions, a more or less complete graphic delineation of them as representing that particular substance might be obtained. When we are able to fully interpret the language or meaning of these curves, we shall learn a very great deal respecting the internal motions and changes of substances, and the conditions of conversion of potential into kinetic energy.

As each curve is a geometrical and quantitative representation of a series of such changes, a complete collection of such curves, yielded by all kinds of aqueous solutions, would constitute an extensive system of representations of the molecular motions of substances somewhat like that of the luminous spectra of bodies; and the magnitudes and harmonic relations of the degrees of electromotive force represented by the

curves will form a very large basis of study for mathematicians, such as the spectra of bodies now afford. The entire subject appears to be nearly as large as that of spectrum analysis, and is not altogether unlike it.

The whole system of curves may be viewed as being in some respects analogous to the absorption-spectra of liquids, and in a less degree to the spectra of gases. The relations between the different curves are probably more complex than those between the spectra of liquids, because the electrodes take part in the action; and still more complex than those between the spectra of gases, because of the influences of the solvent and of the electrodes, and because each dissolved substance is in the liquid state and under the influence of cohesion.

As the magnitudes and forms of the curves are manifestly related to the atomic and molecular weights of the dissolved substances, they are doubtless also related to the periodic series, and in this direction a study of them by mathematicians will lead to the acquisition of new knowledge. And as they reveal the kinetic changes which isomeric and other substances undergo when they pass from one state of chemical equilibrium to another in cases of chemical union, substitution, and decomposition, &c., they are evidently related very intimately to Newton's third law of motion.

With regard to the latter suggestion, in several researches (see "Relative Amounts of Voltaic Energy of Electrolytes," Roy. Soc. Proc. November 1888, xlv. p. 266; "On Loss of Voltaic Energy of Electrolytes by Chemical Union," Proc. Birm. Philos. Soc. December 1888, vi. p. 225; "Relative Amounts of Available Voltaic Energy of Aqueous Solutions," *ibid.* vii. part 1; "Examples of Solution Compounds," *ibid.* and 'Chemical News,' April 1890), I have largely shown, by means of the "voltaic balance" method, that chemical union in definite proportions by weight of substances *whilst in aqueous solution together* is apparently universal; that elements unite with elements, with all kinds of acids, and with all classes of acid, neutral, and basic salts; that acids unite with acids, each with every other one, and each acid with every salt; and salts with each other in almost endless variety; and apparently that all kinds of dissolved chemical compounds, with but few if any exceptions, unite together more or less distinctly, in those definite proportions indiscriminately and without limit of kind, provided no separation of substance by precipitation or otherwise occurs. Also, by repeatedly doubling the molecular weight of a "solution compound" by successive additions to it of other

dissolved substances of equal chemical value, each addition producing a new state of chemical equilibrium, in which chemical action and reaction are equal, I have by the same method shown that chemical union of substances whilst in aqueous solution together extends to large aggregates of molecules of the most varied kind and of considerable degrees of complexity (Proc. Birm. Phil. Soc. vi. p. 225). This universality of chemical union of substances whilst in solution together indicates the existence of an equally general cause of such union, and that cause must be a molecular one.

"The theory most consistent with these facts is a kinetic one, viz. that metals and electrolytes are throughout their masses in a state of molecular movement. That the molecules of these substances, being frictionless bodies in a frictionless medium, and their motion not being dissipated by conduction or otherwise, continue in motion until some cause arises to prevent them. That every different metal and electrolyte has a different class of motions, and that the molecular motion of each substance varies at a different rate by rise of temperature." This theory has been employed by me to explain certain thermoelectric phenomena in electrolytes (see Roy. Soc. Proc. 1883, xxxvi. pp. 54-55). "In accordance with this theory chemical action is an effect of molecular motion, and is one of the modes by which that motion is converted into electric current." "These statements are also consistent with the view that the elementary substances lose a portion of their molecular activity when they unite to form acids or salts, and that electrolytes have usually a less degree of molecular motion than the elements of which they are composed" (*ibid.*).

A kinetic theory must agree with mechanical laws; we cannot create motion or energy, all motion arises from pre-existing motion, every efficient cause of material change is a kinetic one; the immediate source of all chemical change is the latent molecular motion of the combining or mutually acting substances. As neither mere difference of substance, nor union in definite proportions by weight, is in itself an active influence, neither can it be the immediate kinetic cause of chemical change; but as both these circumstances invariably attend chemical union, and no such union occurs without them, we may conclude that they are necessary conditions of the union.

By adopting the above theory, "that electrolytes are throughout their masses in a state of molecular movement; that the molecules of these substances, being frictionless bodies in a frictionless medium, and their motion not being

dissipated by conduction or otherwise, they continue incessantly in movement until some cause arises to prevent them," and associating it with Newton's third law of motion, viz., that "the actions of bodies upon one another are always equal and in opposite directions," we are driven to the inference that what we term "chemical affinity," or the immediate active cause of chemical union, is latent or potential molecular motion and the mutual impact and momentum of the molecules of the uniting substances. When two dissolved substances are brought by admixture of their solutions into mutual contact, a portion of the molecular motion of the one substance is neutralized by an equal amount of opposite motion of the other, and the two portions are converted into free heat, electric current, or other form of energy, and the molecules thus brought into nearer proximity retain their new positions and distances: this agrees with the usual evolution of heat, loss of voltaic energy, depression of electromotive force, and frequent increase of density, which occur during chemical union. According to this view, every dissolved chemical compound is an instance of balanced molecular motion, and it is the neutralized portions of motion which escape as heat and electric current. How far there is any originality in these ideas I leave to other persons to decide.

Many of the facts evolved by the several researches I have referred to point towards the conclusion that measurements of volta-electromotive force and voltaic energy are essentially measurements of "chemical affinity" between the dissolved substance and the positive metal. An analogous idea has already been suggested by other investigators. E. F. Herroun, adopting a view of Helmholtz's, has inferred that "the electromotive force of a voltaic cell is a measure of the actual transformation of free energy," and concluded that it "furnishes a more accurate measurement of the free energy, and therefore of true chemical affinity, than data derived from calorimetric observations" (*Phil. Mag.* 1888, xxvii. pp. 230, 233). The amounts of voltaic energy lost by two substances during their act of chemical union clearly indicate to a large extent the quantities of opposite molecular motion neutralized by their union. For instance, a much larger amount of such motion is neutralized by the union of sodium with chlorine to form sodic chloride than by that of hydrogen with chlorine to form hydrochloric acid; and no doubt, by investigating the losses of electromotive force and voltaic energy attending the chemical union of substances in aqueous solution, we may learn a very great deal respecting the quantitative relations of "chemical affinity" between metals and electrolytes; but

a great obstacle to making accurate measurements of such "affinity" by this method is the unmeasured portion of energy lost by "local action." It may be further remarked that, disregarding "local action," this chemical union and neutralization of opposite molecular motions only occurs whilst the circuit is closed; and that at the instant of closing the circuit, potential energy is converted into kinetic energy, and a multitude of electromagnetic waves of very varied lengths are generated and radiated into space: the conversion of energy, therefore, in this kind of case depends upon closing of the circuit.

The results obtained by varying the strength or the temperature of the liquid at each metal separately support the conclusion that, in an ordinary voltaic cell, nearly the whole of the energy is due to action at the zinc, and but little to that at the platinum; and that the latter acts nearly wholly by obviating the greater counter electromotive force which would occur by using a more corrodible metal, and by diminishing the resistance which a less conducting substance would offer. The mere absence of an obstacle to a change cannot be an active cause of that change; and any substance which takes an essential part in any physical or chemical action, and (like the platinum plate) remains exactly the same in every respect after the action as it was immediately previous to it, cannot have been a real cause of that action, or of any loss or gain of energy attending it. The presence of the negative metal is only a static permitting condition; it enables, without any expenditure of energy on its own part, the opposite potential molecular motions of the positive metal and the liquid to neutralize each other and to be converted into voltaic current.

The method described in this paper is not merely a technical one of detecting substances, nor is it specially fitted for such a purpose; but it is an extensive new department of chemical and molecular research, and a general system of representation by means of geometrical curves, not only of individual substances, but of some of the fundamental changes of molecular motion of substances which are inseparably related to their chief chemical properties; and it will in this way supply mathematicians with a new and extensive series of facts, representing, in terms of electromotive force, the degrees of volta-chemical action of metals and electrolytes upon each other. One of the chief uses of it as a method of research will be to examine the molecular structure and chemical composition of dissolved substances, to detect differences and changes in them caused by heat, light, chemical union, substitution, or decomposition, &c.; and to detect and measure

molecular and chemical differences in isomeric liquids. It may be used to detect and measure the changes gradually produced by light and heat in chlorine water and bromine water, the influence of light upon nitric acid, the degrees of retarding effect of coloured glass screens &c. upon various chemical changes caused by light, the gradual oxidation of a solution of sulphurous anhydride by exposure to air, the spontaneous decomposition of aqua regia, the rate of decomposition of a solution of potassic iodide by chlorine water, the speed of displacement of one acid by another, &c., &c. The examples given and researches suggested are sufficient to indicate the very great extent of the subject.

XLV. The Nature of Solutions.

By SPENCER UMFREVILLE PICKERING, M.A.*

IN the March number of the Journal of the Chemical Society there was published a paper by the present writer, "On the Nature of Solutions," which had been honoured by an adverse criticism from Prof. Arrhenius (Phil. Mag. 1889, xxviii. p. 36) eight months before its appearance *in extenso*.

It is impossible to answer the objections raised by Prof. Arrhenius without giving some account of the work itself; and, as this work is of a character calculated to interest many physicists, it may be advisable to give here a somewhat fuller *résumé* of it than would otherwise be necessary.

Solutions of sulphuric acid formed the subject of the investigation. Series of density-determinations with solutions of different strengths were made at 8°, 18°, 28°, and 38°, each series consisting of 50 to 100 determinations. A still more elaborate series of determinations of the heat of dissolution at 18° were made, as well as some of the heat-capacity of solutions up to 12 per cent. in strength. From the density-results at 18° the contraction on mixing was calculated, and these values treated independently. The density-results, moreover, at the four different temperatures gave the means of calculating the expansion by heat for various intervals of temperature; and, finally, F. and W. Kohlrausch's determinations of the electric conductivity were re-examined, the first examination of them having been made by Crompton (Chem. Soc. Trans. 1888, p. 116).

Different solutions were for the most part used in investigating the different properties, and the total number of determinations made amounted to 600 or 700.

The results were examined by plotting them out, and by

* Communicated by the Author.

differentiating them; the differentiation being performed either on the experimental values themselves or on the smooth curves representing them, generally on both.

For a direct differentiation the difference between the values obtained for the densities, or any other properties, of two solutions was divided by the difference in their percentage composition. The result gave the first differential coefficient; that is, the rate of change in density between these two percentages, or, as it has to be less perfectly expressed, at a point intermediate between the two. If the densities themselves form a continuous and regular curve, the differential deduced from them will form either another continuous curve or a straight line; whereas, if the densities are represented by several different curves, the differential will consist of as many other curves or straight lines. Thus, differentiation was used primarily as a means of rendering more apparent any sudden changes of curvature in the figure representing the experiments; but it generally indicated the nature of the component curves of the latter, since parabolic curves of the second order give straight lines as their first differential. In all cases either the whole or else the greater part of the first differential figures obtained were curvilinear, but, on proceeding to a second differentiation, a rectilinear figure was obtained.

The only case in which the second differentiation could be performed on the first differential values themselves was that of the electric conductivities; in the other cases the magnitude of the errors of the experiments approached too nearly to that of the quantities constituting the second differential to render such a method practicable. In such cases it was necessary to reduce the error by plotting out the first differential points, drawing a smoothed curve through them, and performing the second differentiation on readings taken from this. Prof. Arrhenius objects to such a process: but it is one which every physicist uses to reduce experimental error, and objection might as well be made against taking the mean arithmetically of several determinations at the same point, as against taking the mean of a curve diagrammatically from several determinations along its course. To say that in such a case the mean value taken, or the mean curve drawn, "entirely lacks experimental foundation," and still more, to say that I admit that it does so, is certainly incorrect.

In all cases, except that of the densities and electric conductivities, the first differentiation was applied to the smoothed curve drawn to represent the experiments, as well as to the experimental values themselves: the two first differential figures thus obtained were treated separately and the results compared.

It was found impossible to draw any of the figures obtained with the help of a bent ruler, except in different sections. In some cases these sections cut each other on prolongation, this is so with the heat of dissolution and the expansion-results; in others they meet tangentially, this is so with the first differentials of the densities and conductivities; while in one case, that of the heat-capacities, they do not meet at all. But this want of continuity is probably only apparent. In all cases therefore, except the last mentioned, the whole figure is *continuous*. The fact that it can only be drawn in separate sections does *not* prove that it is made up of so many separate curves. This is only rendered probable by the fact that each section is shown by subsequent differentiation to be within experimental error a parabolic curve, and is proved by the fact that all the very different figures representing the different properties all require to be drawn in the *same* number of sections, and give the *same* number of lines for the second differentials, thus showing changes of curvature in the original figures at the *same* points.

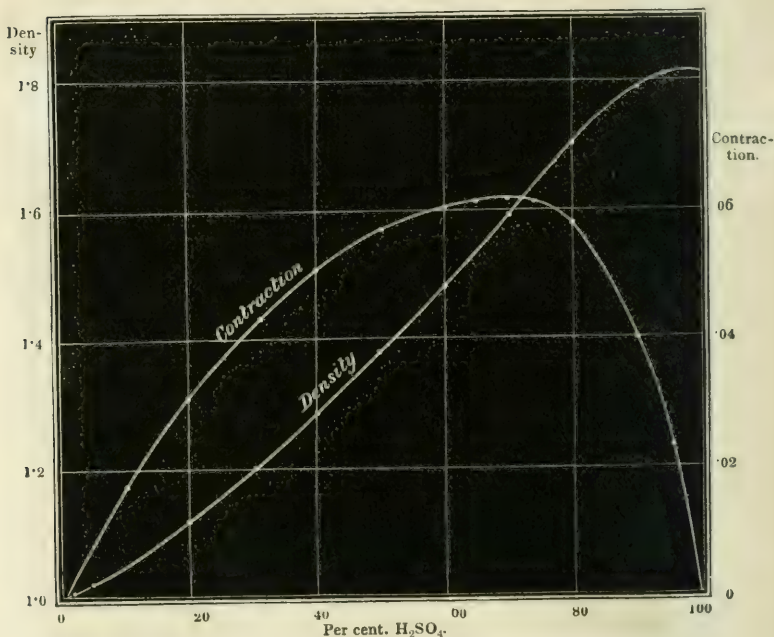
Prof. Arrhenius attacks me on the subject of this smoothing of the curves, remarking that if "Mr. Pickering had 'smoothed' his curve properly he would evidently have removed these angular points or sudden changes of curvature." The question hinges on the interpretation of the word "properly." Prof. Arrhenius seems to think that the "proper" amount of smoothing to be made is such that all sudden changes of curvature should be obliterated; and this, too, in an investigation the sole object of which is to ascertain whether there are such sudden changes or not. I must beg to differ from him. The "proper" amount of smoothing I take to be such as will allow but little more error in the experimental points than the known errors of the determinations, or than that which seems to be the probable error according to the irregularities of consecutive points in the figure. If with such smoothing we are led to conclusions which are obviously false, or which are at variance with the results obtained from independent sources, then and then only must we admit some further unknown source of error, and increase the smoothness of our drawings.

Even excessive and unwarrantable smoothing will not help us in reducing the whole figure to one regular curve, but results only in emphasizing the more marked changes of curvature as the less marked ones disappear. This was found to be so even in the case of the curve for the heat of dissolution of solutions from 5 per cent. in strength upwards; a curve which, of all the instances examined, was that in which the changes were the least marked, and in which the figure presented the greatest seeming regularity.

There can be no question but that the method of analysing results by differentiation presents many difficulties, and must be used with extreme caution ; nor can it be denied that many of the changes of curvature which I consider to be probable are but faintly marked, and are by no means beyond question. This must inevitably be the case if these changes are due to changes in the unstable and partially dissociated hydrates constituting the liquid. Their existence can be established only by the concordance of the indications obtained from many independent sources, and can scarcely be refuted by a hasty criticism (such as Prof. Arrhenius's) of results which had not been published.

Figs. 1, 2, and 3 give rough illustrations of the six experimental curves examined. They show how very different the figures are in the different cases, and how improbable it would be that they should all split up by mere chance into the same number of sections, and exhibit changes at the same points*. Illustrations of the first differentials derived from them would lead to the same conclusion.

Fig. 1.



* Diagrams representing on a larger scale the portions below 10 per cent. would show the differences in a still more striking manner.

Fig. 2.

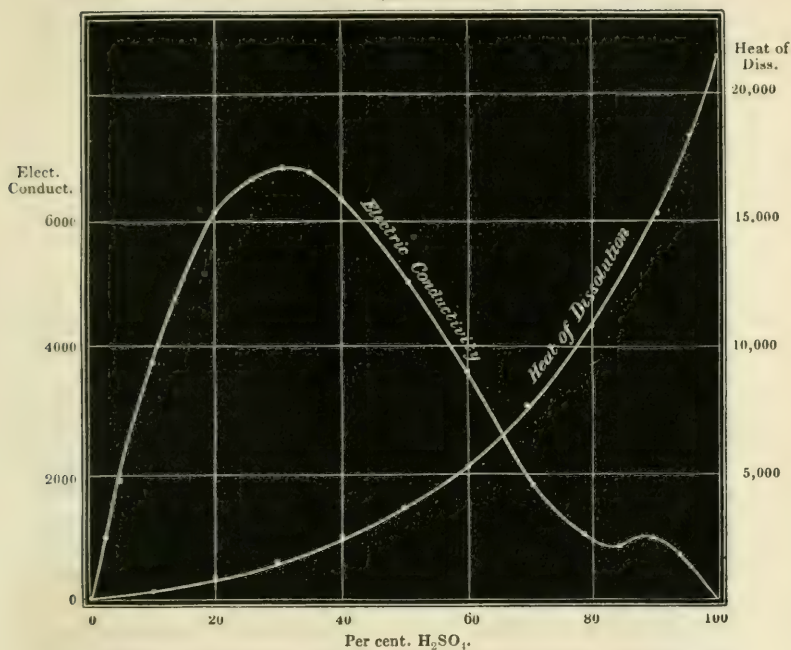
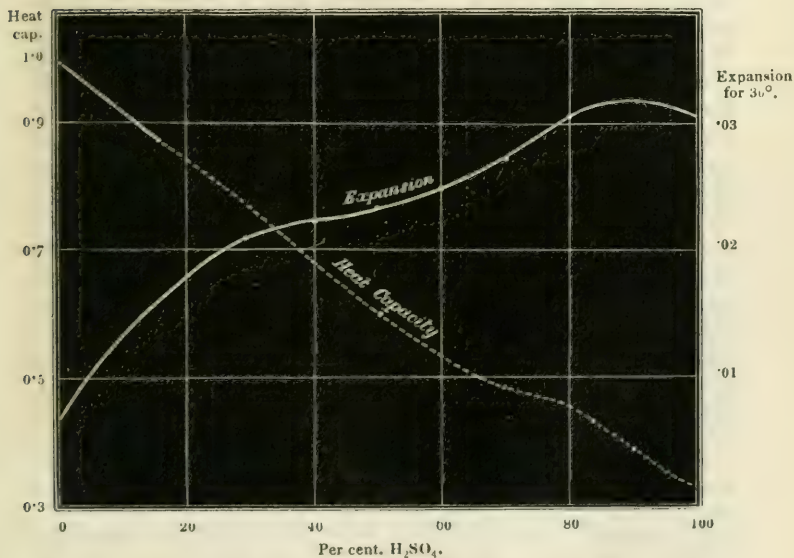


Fig. 3.



NOTE.—Points have been inserted in these diagrams through error; they do not represent the experiments, which are very numerous.

The number of more or less sudden changes of curvature noticed amounted to seventeen, and, of the eight separate series of determinations,

1	showed	1	of the changes,
2	"	1	" "
3	"	1	" "
4	"	4	" "
5	"	1	" "
6	"	7	" "
7	"	2	" "

and it may be fairly stated that in no case did any of the series fail to show a change except through lack of sufficient data.

The concordance, moreover, of the actual position of the changes shown by the various properties was certainly better than might have been expected, considering the great difficulty in determining the exact point at which any two constituent curves cut or touched each other. The average difference between their position as shown by the different individual properties (or by the same property at different temperatures) and by the mean results was only 0.388 per cent., and in only nine cases did it reach or exceed 1 per cent.

Another point which adds confirmation to these results is, that in every case where the hydrate indicated is sufficiently simple to admit of its composition being determined accurately (that is, where a difference of 2 to 11 per cent. would be caused by the addition of one more water-molecule), the changes occur at a point corresponding, within the possible limits of error, to a definite molecular composition*. There are seven such cases available, and the found and calculated values show an average difference of only 0.226 per cent., or about 0.057 H₂O; the maximum reaching but 0.48 per cent., or $\frac{1}{11}$ th H₂O.

A comparison of the density-results at the four different temperatures is very instructive. The first differentials show gradual changes in their general character as the temperature alters, the curvature in the various portions becoming more marked as the temperature is lower; yet, in spite of these alterations in general appearance, the points at which definite alterations in curvature occur remain unaltered†. The con-

* Prof. Arrhenius implies that they do not; but as my found values were not published at the time when he wrote, I do not see how he was in a position to judge.

† In attacking Mendeléeff, Prof. Arrhenius falls into the error of confounding changes in general direction, especially positions of maximum

tractions also are well worth attention. They are deduced from the densities, but form a figure totally unlike the density-curve (fig. 1); and the first differential obtained from them is also totally unlike that from the densities. Yet the second differential figures in the two cases exhibit a similarity of the closest description, not only in general appearance, but in the inclination of almost every line constituting them, as well as in the position of the changes which they show.

Prof. Arrhenius attempts to dismiss the argument based on the concordance of my results from independent sources, by stating "that Mr. Pickering with his multitudinous arbitrary constants can fix the points 'where the breaks occur' just where he chooses." Had Prof. Arrhenius waited to see my results before he attacked them he would have found that, so far from working with "multitudinous arbitrary constants," I worked with no constants at all*; and he would also have found that an attempt to place the breaks by means of constants, or drawn curves, at points other than those at which they really occur led to a signal failure, even when the attempt was made on a portion of the density-curve where the true breaks or changes of curvature were but feebly marked (see p. 78, *loc. cit.*).

The multiplicity of the hydrates as well as the complexity of the highest ones (containing as much as 5000 H_2O) may no doubt prove a stumbling block to others as well as to Prof. Arrhenius. But till we have gained some slight knowledge of the constitution of solutions, it is surely well not to turn our backs on any evidence which may be forthcoming, and brand it as a *reductio ad absurdum* before it is produced. Organic chemistry would be non-existent had it met with such a reception.

Prof. Arrhenius's attack reaches a climax when he states that "Mr. Pickering has deduced from the specific gravity quite different hydrates from Mendeléeff, and from the electric conductivity quite different hydrates from Crompton." This statement is certainly a most unfortunate one; for, though I altogether disagree with Mendeléeff's views as to the nature of the density first differential, and though I think that Crompton's conclusions were scarcely justified by the

elevation, with definite changes of curvature (p. 34). It is obvious that the highest or lowest point in a curvilinear figure may occur in the middle of the most regular portion of it, and such points have nothing to do with the changes of curvature here dealt with.

* I prefer imagining that Prof. Arrhenius really did think that I worked by fitting equations with arbitrary constants on to my curves; but it is rather difficult to reconcile such a view with his previous remarks.

facts at his disposal*, yet the hydrates which I mention as existing include those which both Mendeléeff and Crompton mentioned, thus:—

From Densities.		From Conductivities.		Mean from all sources.
Mendeléeff.	Pickering.	Crompton.	Pickering.	Pickering.
About 84.5	At 84.48	About 84.5	At 84.0	84.24 per cent.
" 73.1	" 73.07	" 73.1	" 73 (?)	73.04 "
" 47.6	" 50.33	" 47.6		49.92 "
	" 18.5	" 18.5		18.92 "
" 3.5	" 4.15	" 3.5	" 3.5	3.99 "

I have mentioned above that the second differential is rectilinear in every case; but I do not by any means think that it has been proved to be absolutely so. The investigation was purely experimental in its nature; and the point of chief importance was that the lines ultimately obtained by differentiation should be straight within the limits of experimental error, for their being so proves that each of them is derived from an independent curve, which, within these same limits, is regular.

XLVI. *On the Shape of Movable Coils used in Electrical Measuring-Instruments.* By T. MATHER, Assistant in the Physical Department, Central Institution†.

IT is with some diffidence that I venture to bring the subject of this note before the Society, because it concerns such a fundamental point in the construction of measuring-instruments having movable coils, such as d'Arsonval galvanometers, electro-dynamometers, wattmeters, &c., that it is almost certain to have been worked out before. However, as the matter is not touched upon in the ordinary text-books, I bring it forward in the hope that it may serve to recall attention to a subject which, judging from the construction of such

* It is not difficult to see how both Mendeléeff and Crompton arrived at partially right conclusions from erroneous or insufficient premisses (*loc. cit.* pp. 79, 86, 125).

† Communicated by the Physical Society: read March 21, 1890.

instruments as are in common use, has been almost entirely ignored.

In a paper "On Galvanometers," by Prof. Ayrton, Dr. Sumpner, and the writer, read before the Society on January 17th, it was pointed out that the coils of d'Arsonval galvanometers should be narrow and long, and that there should be no internal core. Mr. C. V. Boys had evidently arrived at the same conclusion long before the date referred to, for the coil of his radio-micrometer is a proof of this.

The object of this paper is to determine the best shape of the section of the coil perpendicular to the axis about which it turns.

The subject will be dealt with as concerning coils suspended in uniform fields, but similar reasoning may be applied to other instruments in which movable coils are used.

Let the point O (fig. 1) represent in plan the axis about which the coil turns, and assume it is placed in a magnetic field whose direction is perpendicular to A B.

Let P be an element of the section of the coil, then the deflecting moment exerted by unit length measured at right angles to the paper is

$$H C a r \sin \theta ; \quad . \quad . \quad . \quad (1)$$

where H is the strength of field, C the current-density per unit area, *a* the area of the element, and *r* its distance from the axis.

The moment of inertia of the element about O will be

$$w a r^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where *w* is the mass per unit cube.

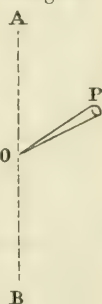
Now in ordinary commercial instruments it is important that the period of oscillation should not be inconveniently long, and that the power consumed by the instrument should be as small as possible ; then, since for a constant period the controlling moment at unit angle must be proportional to the moment of inertia, the problem resolves itself into finding the shape of the section such that the total deflecting moment for a given total moment of inertia is a maximum.

The ratio of the Deflecting Moment to the Moment of Inertia for the element above considered is

$$\frac{H C a r \sin \theta}{w a r^2}, \quad i. \quad e. \quad :: \quad \frac{\sin \theta}{r},$$

since H, C, and *w* may be considered constants.

Fig. 1.



The ratio $\frac{\sin \theta}{r}$ thus is a measure of the efficacy of the element and its position.

If we now draw a curve whose polar equation is

$$r = x_1 \sin \theta,$$

then, as in Maxwell (vol. ii. p. 332), it may be shown that a given length of wire wound within this space is more efficient than if wound outside it. Hence the curve $r = x_1 \sin \theta$, i. e. a circle tangential to A B at O, is the best form of the section of a movable coil, just as in the case of sensitive galvanometers the best shape is given by

$$r^2 = x_1^2 \sin \theta.$$

The complete section is given in fig. 2, and consists of two circles touching at O. The circles C and D have section-lines in different directions to indicate that the current passes in opposite directions in the two.

The problem may be treated in another way; for it resolves itself into finding the shape and position of an area having a given moment of inertia about a point in its plane such that the moment of the area about a coplanar line through the point is a maximum.

Taking the point as pole, and the line as the line of reference, the expression

$$\iint r^2 \sin \theta \, dr \, d\theta \text{ is to be a maximum,}$$

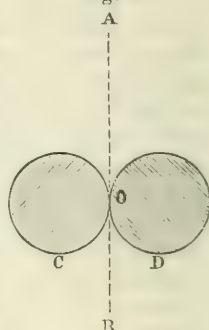
whilst

$$\iint r^3 \, dr \, d\theta \text{ is constant.}$$

This may be solved by the Calculus of Variations with the result above obtained. By this method Dr. Sumpner (to whom the writer suggested the problem) arrived at the solution some time before the author considered the subject from the first point of view.

In order to illustrate the sort of improvement obtained by winding coils to this shape, a table is appended, the first column of which shows various shapes of section, the second column the value of the ratio moment of area \div moment of inertia of area, and the fourth column the deflecting moments of the various shapes all having the unit

Fig. 2.



moment of inertia. From this last column it may be seen that the ordinary Siemens dynamometer type of coil, and those of d'Arsonval's galvanometers and wattmeters, are far from being the most efficacious.

The numbers in column 4 are obtained on the assumption that the coils are long in proportion to their breadth; and when this condition is not fulfilled (as it very seldom is), the numbers would be still further reduced, for the parts of the wire at right angles to the axis of suspension add to the moment of inertia but not much to the deflecting force.

This consideration is of importance where the coils are of sections such as (4), (7), (8), (9); for as the coils are wide, the useless moment of inertia sometimes amounts to one fifth the useful. In such a case as (8) the real numbers representing the efficacy of the coil, as compared with one made to section (1) of the same moment of inertia, would be about 1 to 3. These latter numbers represent approximately the efficacy of the coil of an ordinary Siemens dynamometer reading up to 60 amperes, as compared with that of a coil made to the best shape. It is thus possible to increase the deflecting moment for a given current threefold by changing the shape of the movable coil and arranging the fixed coils to produce the same strength of field as at present used.

Of course the new coil would be heavier than the old one, and would therefore require a stronger suspension which might introduce more vagueness of zero; but as the friction at the mercury-cups is considerable, the necessity for using a stronger suspension would not seriously interfere with the accuracy of the instrument.

It will be noted that in the preceding part of this paper the moment of inertia of the suspended coil has been assumed constant; it is perhaps desirable to give reasons why this assumption is made.

In most instruments having movable coils which are in ordinary use, the current is led into and from the coil either by mercury-cups, or by wires which also serve as the control, or by flexible wires independent of the control.

Taking the first case of mercury-cups, it may be noted that, owing to friction and viscosity, a certain minimum control is necessary to give the requisite definiteness of zero. As time is generally of importance in making commercial measurements, the period of oscillation may be taken as constant. Therefore, as both control and period are determined by circumstances other than those affecting the shape of the coil, the moment of inertia may be taken as constant.

When the current is led into the coil by the torsion-wires,

the smallest size of the latter is usually determined by considerations of heating, and their length is limited by questions of portability, compactness, and resistance. This means that the control cannot be diminished below a certain minimum, and hence, by reasoning as in the last paragraph, the moment of inertia of the coil must not exceed a certain value.




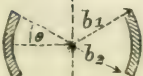
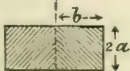

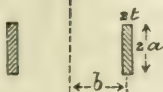
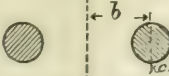

The third case, where the leading-in wires are independent of the control, the conditions are somewhat similar to those in the first case; for the size of these wires is determined by considerations of heating by the current to be measured, and they necessarily possess some viscosity or internal friction, which requires a certain control to give definiteness of zero.

In addition to the assumption of constant Moment of Inertia, the field in which the coil swings is taken to be uniform and parallel; and consequently the reasoning will not apply to radial fields which exist in instruments such as the new d'Arsonval milliamperemeter, having a range of 180° . In such case it would be advantageous to make the coil of a section similar to that in No. 4 (see table), keeping the radius b as small as possible.

The shape given in No. 1 of table cannot be imitated exactly in practice, for insulation-space is required between the two halves, and unless the coil is used in a zero-instrument, parts near the axis might oppose the rest when a considerable deflexion exists. Shapes (3), (5), and (6) are also open to the same objection, but this is easily surmounted by allowing a small space to exist about the axis; in fact some such space is almost necessary to enable the coil to be wound conveniently.

Again, in Siemens dynamometers for fairly large currents it would be difficult to make the coil of the best shape, owing to the space required for the mercury-cups being considerable; but a much closer approximation to this shape than the one often employed could be used.

In ordinary d'Arsonvals, which deflect through a considerable angle, the shape should be modified so that no part of it crosses the line AB (fig. 2) even at the maximum deflexion, for any such part would oppose the rest of the coil. The resulting figure would be lemniscate-shaped. There are some cases, however, such as deflexional dynamometers, where it is advisable to make the coil of such a shape as to cross the line AB when deflected; for then the deflexion would increase less rapidly than the square of the current, and hence the instrument would have a greater useful range for a given length of scale.

	Shape of Section.	Deflecting moment Moment of inertia	Proportions in particular cases.	Deflecting moment per unit Moment of inertia.	Instrument.
1.		$\frac{4}{3b}$	1.02	
2.		$\frac{4 \sin \theta}{3b\theta}$	$\theta = 30^\circ$ $\theta = 45^\circ$	0.91 0.95	
3.		$\frac{8}{3\pi b}$	0.80	
4.		$\frac{4 \sin \theta}{3\theta} \frac{b_1^3 - b_2^3}{b_1^4 - b_2^4}$	$\theta = 19^\circ, b_2 = \frac{12}{13}b_1$	0.44	{ Low-resistance d'Arsonval.
5.		$\frac{3b}{2(b^2 + a^2)}$	$2a = b$ $4a = b$	0.97 0.91	
6.		$\frac{3}{4b}$	0.79	
7.		$\frac{3b}{t^2 + a^2 + 3b^2}$	$a = \frac{1}{5}b, t = \frac{1}{15}b$ $a = \frac{1}{4.8}b, t = \frac{1}{26}b$	0.47 0.38	{ Jolin's High-resistance d'Arsonval. Wattmeter (Ganz and Co.), 60 amperes.
8.		$\frac{b}{b^2 + \frac{c^2}{2}}$	$c = \frac{1}{11}b$	0.40	
9.		$\frac{3b}{t^2 + a^2 + 3b^2}$	$a = \frac{1}{19}b, t = \frac{1}{2.5}b$ $a = \frac{1}{22}b, t = \frac{1}{2.7}b$	0.53 0.49	{ Dynamometer (Siemens), 60 amperes. Dynamometer (Siemens), 500 amperes. Wattmeter (Siemens), 500 amperes.

XLVII. *The Magnetization of Iron in Strong Fields.*

By SHELFORD BIDWELL, M.A., F.R.S.*

IN the Philosophical Magazine for April 1890, p. 293, Mr. Du Bois takes exception to the equation

$$Wg = 2\pi I^2 + HI,$$

which I employed (Proc. Roy. Soc. no. 245, 1886, p. 486) in calculating the curve of magnetization from observations of the pull between two halves of a divided ring-electro-magnet. He objects that a term $\frac{H^2}{8\pi}$ ought to have been added for the mutual attraction of the two half coils of wire.

In point of fact this attraction was found to be quite insignificant, and was purposely neglected. Within the limits of the magnetizing forces used it would have no effect whatever upon the calculated values of I as given in my table. The greatest magnetizing force employed was 585 C.G.S. units, when the weight supported was 15,905 grammes per sq. centim. Substituting these values for H and W , and putting $g = 981$ and $\pi = 3.14$, we get from my equation

$$I = 1530.4.$$

If we add the term $\frac{H^2}{8\pi}$ the solution is

$$I = 1530.2.$$

The value given in my table (in which decimals are discarded) is

$$I = 1530.$$

For the greatest value of H the error is therefore only 2 in the first place of decimals: for smaller values it would of course be less; and it is clear that, whatever the results of my experiments may be worth, they are not affected by the omission to which Mr. Du Bois calls attention.

I regret that, through a mistake, I found fault with Rowland's expression $Wg = \frac{B^2}{8\pi}$. It would certainly have afforded a better and more direct method than my own of arriving at the values of B .

* Communicated by the Author.

XLVIII. *On the Passage of Electricity through Hot Gases.*
By J. J. THOMSON, M.A., F.R.S., Cavendish Professor of
Experimental Physics, Cambridge.

[Continued from p. 366].

Conductivity of Hot Metallic Vapours.

TO vaporize such metals as silver or tin a higher temperature is required than can be produced by the arrangement which sufficed for the substances hitherto described. The method used to determine the conductivity of metallic vapours was as follows:—In a brick made of “ganister” a vertical channel was bored, into which an earthenware crucible was placed; this vertical channel was in communication with a horizontal one which conveyed the flame of a large oxy-hydrogen blowpipe. The terminals conveying the current dipped into the crucible, which was kept full of nitrogen when the metal used was one that readily oxydized. In this furnace silver could be volatilized, and the electrical conductivity of it and most of the metals more volatile than it were tested.

The metals tried were sodium, potassium, thallium, cadmium, mercury, bismuth, lead, aluminium, magnesium, tin, zinc, and silver. Of these the vapours of mercury, tin, and thallium did not seem to conduct at all; at any rate their conductivity is less than that of air; the vapours of the other metals conducted very much better than air, the best conductors being the vapours of sodium and potassium, which conducted even better than iodine.

The difference between the behaviour of the vapours of mercury, tin, and thallium and that of the other metallic vapours is very remarkable. I thought at first it was connected with the behaviour of the salts of these metals when used as electrolytes, as the chlorides of mercury are such bad conductors as hardly to deserve the name of electrolytes, while one of the chlorides of tin is a non-conductor; however, Mr. T. C. Fitzpatrick, who kindly determined for me the conductivity of thallium chloride, found that it was normal, so that the behaviour of the metallic vapours does not seem necessarily connected with the conductivity of the salts of the metal.

The vapour-densities of most of the metals seem to show that the molecules of metals are monatomic; if we suppose the atom is able to possess and give up a charge of electricity, this fact would explain the conductivity of their vapours.

If tin and thallium were found to be exceptions to the rule that the molecule of a metal is monatomic their want of conductivity would be explained. The vapour-density of mercury shows that if its molecule is diatomic all the compounds of

mercury we know are molecular compounds—that is, they contain the molecule of mercury and not the atom; the other alternative would be that the atoms of mercury differ from other atoms in not being charged.

Further Experiments on the Conductivity of Air.

Some experiments, in which the arrangement was slightly altered, seem to throw light on the way in which air conducts electricity: the electrodes, instead of being placed as in the previous experiments in a platinum tube closed at one end and heated by a furnace, were placed at opposite ends of a vertical thin platinum tube open at both ends, which could be made white hot by passing the current from a large number of storage-cells through it. With this arrangement it was found that the current through the hot air was very different according as the upper terminal was positive or negative. When the upper electrode was negative there was hardly any deflexion, but when it was positive there was a deflexion of 70 or 80 scale-divisions. In this experiment there is no appreciable difference of temperature between the top and bottom of the tube; there is, however, a rush of heated air up the tube; and the experiment shows that the positive current of electricity travels much more easily against the current of hot air than with it, indicating I think that the current is largely due to convection and that the particles carrying the current travel from the negative to the positive pole. This seems in accordance with the experiments of Lenard and Wolff already mentioned, for they found that negatively charged platinum disintegrated much more readily than uncharged or positively charged platinum.

When the tube was placed in a bell-jar, filled with one of those gases which conduct electricity well, such as hydrochloric-acid gas, it made but little difference to the current whether the top or bottom electrode was negative, though on admitting the air this difference was at once detected. This indicates, I think, that the main part of the current through air is carried in a different way from that in which it is carried through one of the better conducting gases.

Laws of Conduction through Hot Gases.

It is known that the conduction through hot air does not obey Ohm's law (Blondlot, *Journal de Physique*, 2^e série, t. vi. March 1887). The following experiments, although they cannot lay claim to any very great accuracy, show that the conduction through those gases which conduct electricity well does not depart very much from Ohm's law. The great difficulty in these experiments is to keep the temperature

constant. I found it impossible to do this for any length of time, and so endeavoured to make the experiments as quickly as possible. For this purpose a series of small storage-cells were arranged within easy reach of the observer, and connected in such a way that the number of cells in the circuit could be altered by lifting a wire from one mercury cup and putting it in another. The following are the results obtained in this way with hydrochloric-acid gas at a yellow heat, the observations made within a short time of each other being enclosed in brackets :—

Number of Cells.	Deflexion.	Deflexion per Cell.
9)	35)	3·9)
3 {	13 {	4·3 {
9)	35)	3·9)
3 {	13 {	4·3 {
5)	45)	9·0)
4 {	35 {	8·75 {
2 {	20 {	10·0 {
4)	35)	8·75)
8 {	35 {	4·4 {
4 {	20 {	5·0 {

These experiments seem to indicate that these gases obey Ohm's law.

Influence of the Temperature of the Electrode on the Passage of Electricity through Hot Gases.

The condition of the electrodes exerts a most powerful influence on the passage of electricity through the best conducting gases. This was proved by several experiments in which cold electrodes were suddenly dipped into a gas maintained at a temperature sufficiently high to make it conduct. This experiment was tried in three ways—first, with the platinum tube heated by the furnace ; secondly, with the tube heated by the current ; and, thirdly, with the crucible heated by the oxy-hydrogen blowpipe. In all these cases an arrangement was fitted up which enabled the observer to lift the electrodes (or one of them in the case of the tube heated by the current) out of the hot gas, allow them to cool, and then rapidly replace them. It was always found that however hot the gas might be no deflexion of the galvanometer occurred when the cold electrodes were first placed in the hot gas, and that the time when the mirror of the galvanometer began to move was just the time the electrodes began to glow. The experiment was repeatedly tried both with thick and thin platinum wires, and with thin carbon filaments and thick carbon rods. The cooling of the gas by contact with the electrode does not seem sufficient to explain

this effect, as before the hot gas can be cooled it must come into contact with the electrode ; and as there is a strong up current of hot gas fresh supplies of it are continually coming into contact with the electrode ; so that if the hot gas could give up its electricity to the cold electrode there would be a current through the gas. The difficulty with which cold metals get electrified by hot gases is also shown by the following experiment:—two platinum electrodes were immersed in iodine at a yellow heat, and a piece of platinum foil, whether insulated or uninsulated is immaterial, was arranged so that it could be lowered between the electrodes or raised from the hot gas at pleasure. Initially the platinum foil was out of the iodine and a current was flowing through the hot gas ; the foil was then lowered into the hot gas and at once stopped the current. As soon, however, as the foil began to glow the current recommenced, and the system finally conducted as well as before the introduction of the foil. These experiments seem to show that for electricity to get from the gas into the electrode, or in other words for the atoms to give up their charges to the electrodes, the latter must be at least red hot. Whether this is due to the disintegration of the electrodes at a red heat, or to the increase in the temperature of the electrode producing an increase in that action between the gas and the metal which manifests itself in the case of some gases and metals as chemical action, is a point which I hope to investigate more fully.

Influence of the Material of the Electrode.

Electrodes of platinum, iron, carbon, gold, and aluminium were tried ; the experiments with the aluminium electrodes were not, however, satisfactory, as the electrodes melted as soon as the temperature was high enough to make the gas conduct. The resistance of a conducting gas, such as iodine, seemed practically the same whichever of the first four substances were used. Copper electrodes seemed also to behave in the same way until they got covered with a coating of oxide.

Symmetry of the Conduction.

There does not seem to be in the conduction of electricity through those hot gases which conduct the most readily, that dissimilarity in the properties of the positive and negative electrodes which is found in the discharge through vacuum tubes and in the more closely analogous case of conduction through flames. This was tested by using two electrodes, A and B, which were very unlike in shape and size: in most of the experiments A was a piece of platinum foil, while B was a thin platinum wire. The deflexion of the galvanometer was observed,

first when A was the positive and B the negative electrode; and, secondly, when B was the positive and A the negative electrode. No difference could, however, be observed between the two cases. This is in striking contrast to the results of a similar experiment made by Hankel (Wiedemann's *Elektricität*, iv. p. 891) with different-sized electrodes immersed in a flame; for Hankel found that the deflexion of the galvanometer when the largest electrode was negative was greater than when it was positive in the proportion of 294 to 34. We must remember, however, that though a flame is no doubt very hot gas, the condition of this gas is not nearly so simple as that of the hot gas which was the subject of our experiments. For, in the first place, the temperature of the flame varies greatly from place to place, and, secondly, there seems to be a separation of the electricities in the flame, so that the negative electricity is in one part of the flame and the positive in another. In the hot gas with which we had to deal the temperature was very much more uniform than in the case of a flame, and there was no evidence of the positive electricity being in one part of the gas and the negative in another, as is the case in the flame; this separation of the electricities might easily give rise to a want of symmetry in the conduction.

Another way in which the symmetry of the conduction was tested was by raising one electrode out of the hot gas and keeping it out until it was cool, then suddenly plunging it into the hot gas again. In this case it was found that there was no conduction until both electrodes were glowing, however the signs of the hot and cold electrodes were changed. The same thing was tried in a slightly different way by having two earthenware crucibles at a white heat connected by a strip of platinum foil with one electrode dipping into one crucible and the other into the other; a gas which conducted well was put into one crucible, while the other crucible contained air. No difference in the deflexion of the galvanometer could be detected when the signs of the electrodes were reversed.

Polarization.

A great many experiments were made with various hot gases, such as iodine, hydriodic acid, hydrochloric-acid gas, and the vapours of sodium and potassium, to see if the passage of the electricity through these gases produced any polarization of the electrodes. The result of these experiments was that when all the sources of disturbance were eliminated no effect of this kind could be detected. In the first set of experiments a commutator was used which first sent the current through the gas, the galvanometer being out of circuit; on

reversing the commutator, the battery was thrown out of circuit and the galvanometer in. In this case no deflexion of the galvanometer was obtained though the current from 150 Daniell's cells had passed through the gas for several minutes. As, however, it seemed possible that the polarization of the electrodes, if it existed, might have disappeared in the short time taken to reverse the commutator, another experiment was tried. In this a very large resistance, formed by rubbing graphite on a piece of ebonite, was put in parallel with the hot-gas resistance. The graphite resistance was so large that practically all the current went through the hot gas; and the galvanometer-needle was so still that any disturbance of it could easily have been detected. On breaking the battery circuit, however, no kick of the galvanometer could be detected, though as before the current from a battery of 150 Daniell's cells had been flowing through the hot gas for several minutes.

Electrolytic polarization is connected with the work required to split up the electrolyte into its ions. In the case of the hot gas on our supposition the molecules are already split up into their ions, so that the absence of polarization in this case is not inconsistent with its presence in electrolysis.

At first sight it might seem that the fact that those gases which dissociate conduct electricity on a scale altogether different from those which do not, points to the theory that the conductivity of electrolytes is due to the presence in the liquid of free ions, the number of these being very large, in some cases so large that it corresponds to a dissociation of more than 90 per cent. of the electrolyte. I think, however, that a closer examination of the case will lead to the opposite conclusion. Let us take the case of iodine for example, which at high temperatures is known to dissociate largely. The specific resistance of iodine vapour at a yellow heat is comparable with $\frac{1}{10}$ of a megohm, or about the same order of magnitude as that of glass at the temperature 300°C . This resistance is enormously greater than that of a solution of potassium iodide for example, containing the same number of molecules per unit volume as the gas; on the hypothesis of free ions, with definite electrical charges, we should expect the opposite result, as we cannot suppose that the resistance to the motion of the free ions is as great in the gas as it is in the liquid. The agreement between the conductivity of a salt solution and the effect produced by the presence of the salt on the freezing-point and vapour-pressure does not seem to be at all a conclusive argument as to the existence of these free ions; for exactly the same result would follow on the hypothesis that the conductivity was proportional to the chemical

action between the salt and the solvent, if the thermal effect accompanying this action were to follow the logarithmic law, that is if the thermal effect produced by increasing the quantity of water by unity were inversely proportional to the quantity of water already present.

From the consideration of the preceding experiments we may deduce, I think, the conclusion that it is the atoms, as distinct from the molecules, which are instrumental in carrying electricity from one place to another, and that the molecules are electrically inactive.

Many interesting questions arise as to how the atoms effect this transference of electricity. Does each atom, for example, carry a charge equal to that (10^{-11} in electrostatic units) deduced from electrolytic considerations, and is this charge unalterable?

In this connexion it is important to notice that all that electrolysis teaches us is that each ion which comes up to the electrode receives from it a definite and calculable charge. It does not, however, give us any information about the charges on ions under other circumstances. If we adopt the view enunciated by v. Helmholtz, in the Faraday lecture, that chemical forces are electrical in their origin, we must suppose that the charges on the atoms are susceptible of change, for the hydrogen ascending from the kathode is in the molecular condition, each molecule consisting of two atoms with equal and opposite charges; the charges on one or both of these atoms must have undergone some change, for when the atoms were in contact with the kathode they were presumably in the same electrical condition. It seems probable that when two atoms come very near together they may affect the charges on each other, the gain of the one being equal to the loss of the other. To fix our ideas we may imagine that the electric charge is measured by the momentum corresponding to some coordinate helping to fix the configuration of the atom, and that when two atoms come quite close together their momenta change, the one gaining as much as the other loses.

If we had a collection of charged atoms of this kind, even though the charges might not all be numerically exactly equal, if combination began the molecules formed would be electrically neutral, for the potential energy, other things being the same, is a minimum when this is the case.

It may perhaps give a clearer idea of the theory we are considering if we take the particular case of a charged metal plate and consider what are the conditions under which it can lose its charge. According to our view the charge on the plate implies the presence of atoms of the metal of which the plate is made; and in order for the plate to lose its charge, these charged

atoms must be neutralized by combining with equal and oppositely charged atoms, or perhaps by acting on atoms quite close to them. In any case, for the charge to diminish there must be atoms in the neighbourhood of the plate. If the electric intensity in the neighbourhood of the plate is sufficient, these may be supplied by the splitting up of the molecules by the electric field, and we have the electric discharge; or the atoms may, as in our experiments, be supplied by the dissociation of the molecules by heat. Besides the mere existence of the atoms, the conditions must be such that they come into intimate contact with those of the metal.

A possible way of supplying the atoms necessary to get rid of the charge might be by chemical action of the gas on the electrodes. In this case, however, the leak would be much less than if the whole body of the gas contained free atoms, as in the preceding experiments. I tried some experiments on the conductivity of gases which slowly acted on the electrodes, and also of mixture of gases, such as chlorine and H_2S , which slowly act upon each other, these experiments being made at a temperature less than 100°C . I was not able to be sure of any leak by the galvanometer method, and a similar remark applies to an experiment when the electrodes were made white hot while the gas was cold. It must be remembered that the galvanometer method, although more convenient, is not nearly so sensitive as the electrostatic method; so that these results only show that the conductivity in these cases is not comparable with that of some hot gases. It is known that the leak from a hot platinum wire can be detected with an electroscope.

The connexion on this view between the conductivity of metals and their tendency to assume the atomic condition, which is exemplified by the abnormal vapour-densities of these substances, will at once occur to the reader.

Unsaturated Compounds.

It is very interesting to see whether the molecules of unsaturated compounds possess the same electrical properties as atoms or not. I accordingly examined the electrical properties of two gases, which on the ordinary electrical theory of chemical action would be unsaturated, viz. NO , and ozone, prepared by passing air through a tube in which the silent discharge was taking place. I could not ascertain that these gases behave in any way differently from air. They transmit electrostatic induction: for example, a gold-leaf electroscope will work perfectly well inside a glass vessel filled with NO or ozone, and the leaves will be attracted by an electrified body outside the electroscope. A current from a battery containing a moderate number of cells will not pass through

these gases when cold, nor will a current go through NO when the electrodes are made to glow by insulated batteries; so that in this case the want of conductivity cannot be due to the electricity being unable to get from the gas into the electrodes. These experiments show that the molecules of those gases are electrically neutral. This cannot be the case if we suppose the atoms to be charged with definite and equal quantities of electricity; for if this were so, O_3 , the molecule of ozone, would have a resultant charge. We must therefore either suppose that the charges on the atoms are capable of variation, or else that the resultant effect of the charges on the atoms is to be got by combining the charges like vectors and not like scalars, for if this were so it would be easy to explain the neutrality of O_3 .

XLIX. *Notices respecting New Books.*

Algebra: an elementary Textbook for the higher classes of Secondary Schools and for Colleges. By G. CHRYSTAL, LL.D. Part II. (Edinburgh: Black. 1889. Pp. xxiv+588.)

IN this splendid volume we have the fulfilment of the Author's promise, and, we presume, the completion of his labours upon Elementary Algebra. Of what sort this work is will be recognized by readers of the first volume when they are assured that the present instalment is even more worthy of praise, if that be possible, than its predecessor. There is no shirking of difficulties, for our Author is a past master of his subject; and from a large acquaintance with what has been written upon it, both recently and long ago, is able to bring forth things new and old out of his ample store. Still he does not exhibit his wares from a vain desire to show off, but has ever an eye to what will be useful to the student subsequently. Hence in his chapter on Probability he omits "matter of doubtful soundness, and of questionable utility," and fills the place usually occupied therewith with "a useful exposition of the principles of actuarial calculation." There is a very full analytical Table of Contents which puts the student easily in possession of the heads of the matters discussed in the text. There are, as before, valuable historical notes, and to crown all there is a full Index of Names of Mathematicians whose works have been cited in the two volumes. Much time has been devoted to the construction of the work; this is evident on the most cursory examination, but we feel convinced that Dr. Chrystal has an ample reward in the admiring gratitude of his readers. They feel that if the Author has given so much of his valuable labour to make the path, if not smooth for them, at least plain, and has collected so many objects of interest for their inspection, it is but meet that they should not flinch from doing their best to master what he has put before them. Our Author, it is well known, has clear and pronounced views on the teaching of Mathematics, and in his preface he comments on points to which we will now briefly refer. The practice of "hurrying young students into

the manipulation of the machinery of the Differential and Integral Calculus before they have grasped the preliminary notions of a *Limit* and of an *Infinite Series*" he pronounces to be to a large extent an "educational sham," which is a "sin against the spirit of mathematical progress." Hence, after devoting the two opening chapters to the subjects of Permutations and Combinations, and the general theory of Inequalities, he discusses very fully and admirably in the following two chapters the doctrine of Limits and the convergence of infinite series and of infinite products: these are followed by chapters applying the previous results to Binomial and Multinomial series for any index, and to Exponential and Logarithmic series. All this forms a good introduction to the theory of Functions, such as has been opened up by the labours of Cauchy, Riemann, Weierstrass, and others, and will enable the student who assimilates the results to get an intelligent hold upon the Calculus. This account of the function-theory is further illustrated in other three chapters, in which the Author treats of Graphs of the circular functions, Riemann's surface, hyperbolic functions, Gudermannian functions, the numbers of Bernoulli and Euler, and a host of other choice matters, succeeded by explanations of the method of finite differences, Recurring series, and a group of miscellaneous methods. The concluding five chapters are devoted to Continued Fractions, properties of Integral Numbers, and, as we have already mentioned, Probability. This is a very scanty account of much admirable work, but the analysis of one chapter would occupy too much space. The dip we have made here and there (on the *ex pede Herculem* theory) will be enough to assure those of our readers who have not yet got the book that there is a rare treat in store for them if they will but get it. The "get-up" and other features make the volume a handsome addition to one's book-shelf.

L. Intelligence and Miscellaneous Articles.

ON ELECTRICAL OSCILLATIONS IN STRAIGHT CONDUCTORS.

BY PROF. STEFAN.

IF a variable current is transmitted through a wire which is surrounded by a concentric metal tube, a current is induced in this tube. The direction and magnitude, as well as the distribution in the tube, may be directly deduced from the principle of least magnetic energy when the current in the wire is supposed to be given. The minimum of this energy is obtained by the following arrangement of the currents:—The central current is condensed in an infinitely thin layer on the surface. The induced current flows in an infinitely thin layer on the inner surface of the tube, and has at any instant the same intensity as the current in the central wire, but the opposite direction. With this arrangement magnetic forces are only effective in the space between the surface of the wire and the inner surface of the tube. The interior of the wire as well as that filled by the mass of the tube, and in addition the whole external face, are free from magnetic forces.

The tube laid round the wire neutralizes also its inductive action in the entire outer space; it forms a complete screen for the inducing as well as the magnetic forces of the wire surrounded by it. The screening action of the tube, according to this view, consists in the fact that the actions of the central current are neutralized by those of the induced current in the tube.

This case is completely analogous to the electrostatic problem of the distribution of electricity on two concentric cylinders, of which the inner one is insulated and the outer put to earth. In like manner the problem of the distribution of the current, even when the wire and the tube are not concentric, and have other than circular section, is to be solved by the analogous problem in electrostatics. The screening action of the tube is complete even under these altered conditions.

The influence of the screening-tube on the velocity of propagation of waves in the wire results in the following manner:—By restricting the magnetic field to the space between the wire and the tube, the self-induction in the wire is considerably diminished. For a circular section and concentric positions this diminution may be easily given. An increase of the velocity of propagation corresponds to this, if the capacity is almost the same, which, according to electrostatic rules, is the case so long as the tube is insulated. But if this is put to earth, the capacity of the inner wire is increased in proportion as the self-induction is diminished, and consequently the velocity of propagation remains unchanged.

The capacity may, however, be considerably increased by filling the space between the wire and the tube with a stronger dielectric than air; by interposing, for instance, a glass tube between the wire and the tube. This glass tube has no influence on the self-induction, but the capacity is almost doubled. The velocity of propagation sinks thus in the ratio of $\sqrt{2}$ to 1. Sir W. Thomson has already remarked this influence of the insulating medium on the velocity of propagation.

If a current is divided at two equal wires, one of which is surrounded by a tube but the other not, the former will take a far greater part of the current than the second, owing to the greater diminution of the self-induction, which is due to the enveloping tube.

If, now, a second straight wire is placed parallel to a conductor through which a current is passing, the primary current distributes itself on the surface of the first, and the induced one on that of the second conductor, in the same way as a given charge would be distributed on the first, and the induced one on the second conductor, if the latter were put to earth. If the first conductor has a circular section, the current is not distributed uniformly over its surface, but has a greater density on the side nearest the second conductor than on that away from it. If this condensation is visible, as in a Geissler's tube, it presents the phenomenon of an attraction of the current towards the approached conductor. As a matter of fact, there is an electrodynamical repulsion between the conductor of the primary current and the approached conductor, which is observed at

a higher degree of rarefaction, and therefore at an increased resistance, in which the apparent attraction no longer occurs.

A conductor also which does not encircle the one carrying the current partially exerts a screening action, and to a greater extent the longer it is. Prof. Hertz has shown that a system of parallel stretched wires may also act as a plane-shaped conductor. Such a system of wires can, however, only exert a screening action if the primary current can induce currents in those wires; such wires form, therefore, no screen when they are placed at right angles to the primary conductor. Induced currents form also an essential condition that a conductor can reflect inducing actions. The reflected actions are the actions of the currents which are induced on the surface of the reflecting conductor.—*Wiener Berichte*, January 16, 1890.

ON THE OSCILLATIONS OF PERIODICALLY HEATED AIR.

BY DR. MARGULES.

Prof. Hann's investigations on the Daily Oscillation of the Barometer led the author to calculate the variations in pressure which result from periodical changes of temperature in the air. Plane waves of temperature progressing in a plane stratum of air produce pressure-waves of equal period, the amplitude of which is greater the nearer the velocity of propagation of the constrained approximates to that of the free vibrations. If the atmosphere were cut into a great number of zones each of which was traversed by a daily wave of temperature, the zones near the equator would have waves of pressure in which the maximum coincided with the maximum of temperature; near the poles the phases would be opposite, at 50° of latitude the amplitude would be very great, and in two adjacent zones of opposite phase. The magnitude of the differences of pressure between two separate zones which thus results shows that the transference to annular spaces of the calculation which holds for plane waves is not sufficient, and that the movements of the air upon the globe must be calculated without diaphragms, if waves of temperature travel from meridian to meridian. The calculation for the spheroid at rest shows, as already demonstrated by Lord Rayleigh in a recent paper (*Phil. Mag.* February 1890), that the semidiurnal waves of pressure on the earth are far smaller than the diurnal ones, even if the corresponding waves of temperature are of the same amplitude. But the semidiurnal variations of temperature (which are obtained by decomposing the daily curve of temperature by the method of periodic series) are small compared with the diurnal ones. How, notwithstanding this, the relatively large semidiurnal variations of pressure may be explained, has incidentally been indicated by Sir W. Thomson. The calculation for the rotating spherical shell, made in a manner analogous to that for Laplace's calculation of ebb and flow, confirms Thomson's supposition. Small semidiurnal variations of temperature are sufficient, with a corresponding choice of the mean temperature, to produce very great variations of pressure.—*Wiener Berichte*, March 6, 1890.

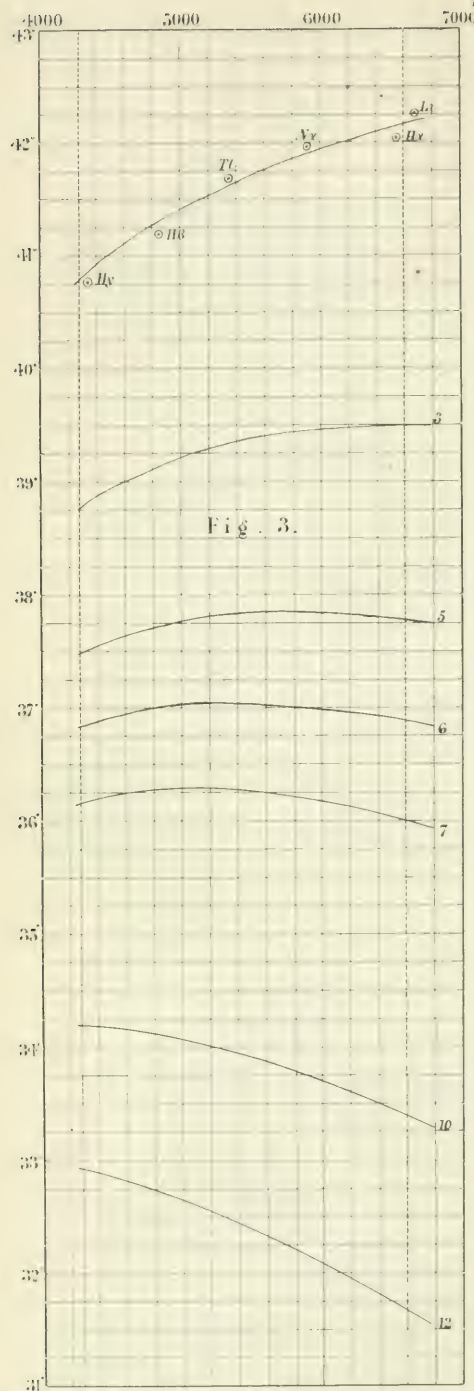
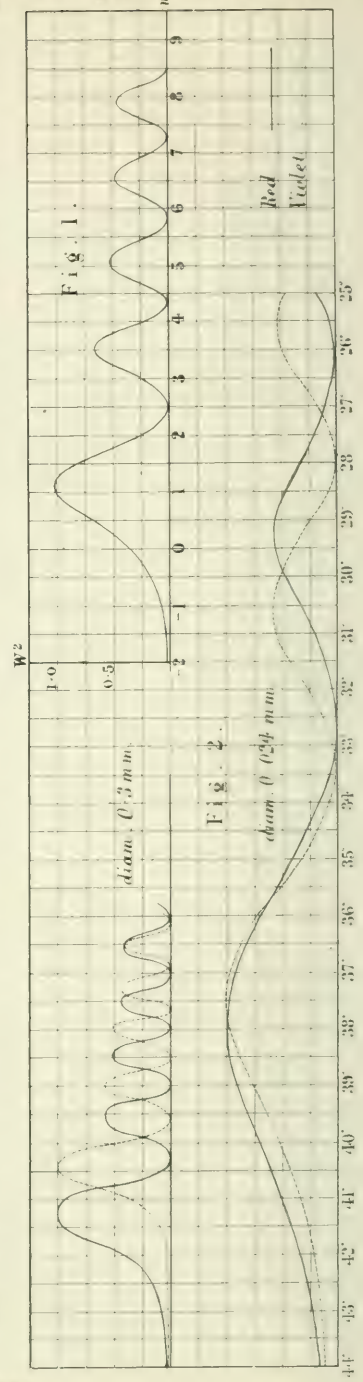


Fig. 3.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

JUNE 1890.

LI. *The Theory of Fog-Bows.* By JAMES C. McCONNEL,
M.A., *Fellow of Clare College, Cambridge*.*.

[Plate X.]

THE supernumerary bows often seen within the ordinary rainbow received their first explanation, bordering on the truth, from Thomas Young†. In the principal plane through the centre of the drop, as we increase the angle of incidence from zero to a right angle, the deviation of the rays from their original direction at first diminishes, gradually reaches a minimum, and finally increases again. So for any deviation slightly greater than the minimum there are two emergent rays which have travelled paths of slightly different length and are in a condition to interfere. By the interference of such Young supposed the supernumerary bows to be formed.

Now the wave theory in its essence knows no such thing as rays, and they should be regarded merely as convenient symbols for obtaining approximate results when the wave-surfaces are spherical. In all ordinary cases the wave-surfaces may be treated as spherical, but the rainbow is an exception. The wave-surface of the emergent light changes the sign of its curvature at a point corresponding to the ray of minimum deviation; and thus we have diffraction phenomena, depending merely on the peculiar shape of the wave-surface, without any limitation by screens.

* Communicated by the Author.

† Phil. Trans. 1804; or *Encyc. Brit.*, eighth edition, art. "Chromatics."
Phil. Mag. S. 5. Vol. 29. No. 181. June 1890. 2 N

On these lines Sir George Airy* worked out the true theory; showing not only that the light attains a principal maximum in one direction and a series of lesser maxima in neighbouring directions, but also that the principal maximum does not, as Young supposed, fall exactly in the direction of minimum deviation. The amount of its divergence is dependent on the diameter of the drops. The smaller the drops the smaller is the rainbow, and the further are the supernumerary bows separated from the principal bow and from each other.

When the sun is shining on fog or mist, a bow is often seen differing considerably in appearance from the ordinary rainbow—far broader and, though quite bright, nearly colourless. The breadth may be as much as 6° or 7° instead of $1\frac{1}{2}^\circ$ as in the rainbow, and the colouring seldom surpasses “a faint dull red and orange at the outer border and a slight blue tinge” at the inner. The mean radius is a few degrees less than in the rainbow. Verdet† considers this to be a degraded form of the primary rainbow. According to Airy’s theory the radius would be diminished by smallness of the drops; and Verdet attributes the whiteness (1) to the faintness of the illumination, and (2) to the irregularity in size of the drops. There can be little doubt that the main contention is correct, and more satisfactory reasons may be adduced for the want of colour, as we shall see.

At the top of Ben Nevis there are many opportunities for seeing fog-bows, and the observers there are provided with a special instrument‡ for taking their angular dimensions. Mr. Omond has kindly sent me a list of such observations from May 1886 to October 1887, extracted from the Proceedings of the Royal Society of Edinburgh for 1887. Those relating to fog-bows are quoted below. The temperatures (Fahr.) were taken in a Stevenson screen at the times named.

(1) “October 7, 1886. Temp. $39^\circ\cdot8$. At 12 h. a solar fog-bow. No colours, only a broad white band.

Radius to inside of bow	$36^\circ 20'$
„ outside „	$43^\circ 36'$

(2) “October 22. Temp. $31^\circ\cdot5$. Fog-bow seen at 11 h. 25 m. Colours as in fig. 1.” [They are, from the outside inwards, brownish red, pale green, pink, light blue, red,

* Trans. Camb. Phil. Soc. vi. p. 379; viii. p. 595.

† *Leçons d'Optique Physique*, i. p. 422.

‡ This instrument, named a stephanome, consists of a graduated bar, at one end of which the eye is placed and on which slides a cross bar carrying certain pointed projections. With its aid faint objects, for which a sextant would be useless, may be measured to within $5'$.

light blue, red.] “No measurements were got. The pink was a badly-defined space, not a true band. A coloured glory was seen at the same time.

(3) “November 12. Temp. $27^{\circ}9$. Double fog-bow seen at 13 h.; outer bow white, inner bow red and blue, red being inside.

(4) “November 16. Temp. $22^{\circ}0$. Fog-bow seen at 11 h.; red outside and white inside. A fainter bow was seen inside this one at times.

(5) “December 16. Temp. $15^{\circ}7$. Glory and fog-bow seen at 15 h., too fleeting to measure. The glory was double with reds outside; the fog-bow a broad whitish band, with occasionally another bow inside it more sharply defined and coloured, but the order of its colours was not observed.

(6) “December 26. Temp. 18° . At 12 h. 30 m. misty glory and double fog-bow seen; outer bow had red outside and inner bow red inside. No measurements got.

(7) “December 30. Temp. $24^{\circ}2$. Double fog-bow seen at 11 h. Red outside outer bow and inside inner bow. The following rough measurements were got:—

Radius of outside of outer bow	. .	$41^{\circ} 22'$
„ middle „	. . .	$39^{\circ} 20'$
„ inside „	. . .	$36^{\circ} 36'$
„ outside of inner bow	. .	$34^{\circ} 44'$
„ inside „	. . .	$32^{\circ} 20'$

The first and last measurements give the radii of the outer and inner red respectively.

(8) “January 2, 1887. Temp. $20^{\circ}3$. Lunar fog-bow seen at 18° h. Radius about $38^{\circ} 40'$.

(9) “February 6. Temp. $22^{\circ}5$. Lunar fog-bow seen at

2 h.	Inside radius	. . .	$33^{\circ} 56'$
	Outside „	. . .	$40^{\circ} 20'$

(10) “February 13. Temp. $28^{\circ}1$. Double fog-bow seen at 12 h. Trace of red outside outer and inside inner bow. No measurements got.

(11) “April 5. Temp. $16^{\circ}3$. Fog-bow (faint) seen at 3 h.” [Lunar.]

(12) “June 29. Temp. $42^{\circ}0$. Fog-bow, occasionally double, observed at 5 h. and 6 h.

(13) “July 21. Temp. $46^{\circ}5$. A double fog-bow seen at times. Red inside inner bow and outside outer bow; the rest of the bows were white.

(14) “August 19. Temp. $37^{\circ}8$. Fog-bow seen at 9 h. 45 m.

(15) “September 18. Temp. $45^{\circ}0$. Fog-bow observed at 13 h. 30 m., measuring $35^{\circ} 16'$ (to inside of bow?).

(16) "October 4. Temp. $43^{\circ}0$. Lunar fog-bow at 23 h. Radius to inner edge (about) $38^{\circ}5'$.

(17) "October 5. Temp. $36^{\circ}1$. At 2 h. fog was beginning to blow across the hill-top, and on it a distinct lunar fog-bow was seen with traces of a faint second bow outside it. The following measurements of the inner bow were got:—

Radius to inside edge	. . .	$35^{\circ}4'$
„ outside edge	. . .	$41^{\circ}0'$

"Temp. $34^{\circ}3$. A similar lunar fog-bow was seen at 3 h. ; there appeared to be a faint trace of red about the outer edge of the inner bow.

"Temp. $34^{\circ}1$. The fog-bow was seen again at 4 h. and 5 h. The following measurements were made at 4 h. :—

Radius to inside of inner bow	. . .	$36^{\circ}3'$
„ outside of inner bow	. . .	$41^{\circ}0'$

(18) "October 15. Temp. $25^{\circ}9$. At 14 h. double fog-bow and glories observed ; no measurements got."

A remarkable feature of this list is the number of double fog-bows. Out of eighteen bows no fewer than ten were double. In one case (17) the outer bow was probably a form of the secondary rainbow ; for the inner bow, according to the measurements, extended at one edge almost up to the normal radius of the primary rainbow. But in the other case, in which measurements were taken (7), both bows were within this radius, and in (3), (6), (7), (10), and (13) the inner bow had the red inside. Assuming that the two bows are the primary bow and its first supernumerary, the reversal of the normal order of the colours in the inner bow is a direct result of Airy's theory, and my main object in writing the present article is to point this out.

The divergence of the principal bow from its normal position, and of the first supernumerary from the principal bow, depends on the ratio of the radius of the drops to the wave-length of the light. As it is greater with a given kind of light the smaller the drops, so with given drops it is greater the greater the wave-length. For red light it is greater than for blue. As long as it is small for both, it only brings the red bow rather nearer the blue ; but, when it is greater, it may bring the red bow to coincide with the blue ; and it may become so great—with the first supernumerary at any rate—as to put the red bow well within the blue. This is the essence of the explanation ; but, to treat the matter properly, a fuller statement of Airy's results is required.

The intensity of the light in any direction is proportional to the square of the expression

$$W = \int_0^\infty \cos \frac{\pi}{2} (w^3 - mw) dw, \quad (1)$$

where m is connected with the angular separation χ of that direction from the geometrical bow by the equation

$$\chi = qm \frac{\lambda^{\frac{2}{3}}}{a^{\frac{2}{3}}}; \quad (2)$$

q was left by Airy an undetermined constant. It has recently been shown by Boitel* and Larmor† that, for the primary bow,

$$q^6 = \frac{9}{4096} \frac{4 - \mu^2}{(\mu^2 - 1)^3}, \quad (3)$$

Thus q , which may be treated as constant for different colours, = 0.465 nearly.

Everything turns on the value of W^2 . Airy, calculating by quadratures, found that, for negative values of m , W^2 , starting from a small value at $m=0$, rapidly and continuously decreases and becomes very soon insensible; but on the positive side W^2 has an infinite number of fluctuations, vanishing between the successive maxima. Selected values are given in the following table:—

	m .	W^2 .
	—4.00	0.000009
	—1.00	0.0745
	0.00	0.357
	0.80	0.940
1st maximum ...	1.08	1.006
	1.20	0.995
	2.50	0.000
2nd maximum ...	3.47	0.615
	4.36	0.000
3rd maximum ...	5.14	0.510
	5.89	0.000
4th maximum ...	6.58	0.450
	7.24	0.000
5th maximum ...	7.87	0.412
	8.48	0.000

* *Comptes Rendus*, 1888; or *Phil. Mag.* August 1888. Boitel points out that Airy's equation to the wave-surface is only a first approximation, and has found experimentally some small discrepancy between theory and observation which he attributes to this. But Larmor's analysis of Miller's observations on fine jets of water shows no discrepancies greater than 4', up to $\chi=10^\circ$.

† *Proc. Camb. Phil. Soc.* vi. p. 283 (1888).

Airy's calculation extended from $m = -4$ to $m = +4$. Outside these limits the calculation by quadratures becomes almost impracticable, but Sir George Stokes* has found a rapidly convergent series for W in descending powers of m . From this follow simple approximations. For the dark bands $m = 3(i - \frac{1}{4})^{\frac{2}{3}}$, where i is given the values 1, 2, 3... successively.

For the maxima, $m = 3(i - \frac{3}{4})^{\frac{2}{3}}$ and $W^2 = \frac{2}{\sqrt{3m}}$. These are accurate enough for most purposes when $i > 1$.

The variations of W^2 with m are exhibited graphically in Pl. X. fig. 1. It will be observed that the first band is much broader as well as higher than the others, and that the intensity at $m = \chi = 0$ is by no means negligible. Thus, putting the question of colour on one side, the effect of diminishing the size of the drops is to spread out the principal bow in an inward direction, leaving its outer edge but little affected. After the third band the brightness diminishes very slowly. Even the 30th maximum at $m = 28.5$ has the value $W^2 = 0.217$. Of course the irregularity of the drops would prevent any colour-effects or distinct bands as far out as this, and we should only look for white light; and this is exactly what is observed. The space within the primary rainbow is strikingly brighter than that outside; and Mr. Backhouse describes the glare within a fog-bow he witnessed as being not much inferior in brightness to the bow itself.

Some idea of the colour-effects in two cases may be gleaned from fig. 2. I have taken as the representative red and violet of the spectrum, light of wave-lengths 0.000615 millim. and 0.000455 millim. It happens that the radii of the geometrical bows for these colours are 42° and 41° . The curve representing the brightness of the red is set out in accordance with equation (2), 42° being taken as equivalent to $m = \chi = 0$. In the curve for violet, which is dotted in the figure, 41° is taken as equivalent to $\chi = 0$. The upper pair of curves represent the case when $2a$, the diameter of the drops, is 0.3 millim., the lower pair the case when $2a = 0.024$ millim. In the former the drops are of about the size adapted to give the most vivid colours possible in the principal bow and the first two supernumeraries. When the drops are very large, say 5 millim. in diameter, it is true that the principal maxima for red and violet are better separated, but the principal violet maximum gets entangled with a number of the smaller red maxima. Thus, when we take

* Trans. Camb. Phil. Soc. ix. 1850, or Collected Papers, ii. p. 329.

the blurring due to the finite diameter of the sun into account, it is clear that the violet would be far more diluted with red and other colours than in the case illustrated. There is an intermediate stage in which the green would reach its maximum purity, but the violet would be poor.

This first case would be realized in a rainbow formed by unusually fine drops. The other case might be described by an observer as a double fog-bow, the outer bow being broad—extending from $42\frac{1}{2}^\circ$ to $34\frac{1}{2}^\circ$ —and colourless except for a reddish tinge on the outer edge; and the inner bow—extending from 32° to $27\frac{1}{2}^\circ$ —being brightly coloured with the red inside. This figure shows that the whiteness of the outer bow is sufficiently explained (1) by the immense breadth of the bow even when formed by homogeneous light, and (2) by the approximation of the red to the violet maximum. In this case they are about $\frac{1}{4}^\circ$ apart. The fact of the third bow being so seldom observed can hardly be due to its faintness, so we must attribute it to irregularity in the size of the drops.

Thus far we have only treated of two special wave-lengths. In fig. 3 may be seen the relative positions of all the different colours in bows of various radii. The abscissæ are wave-lengths and the ordinates radii of the bows. The top curve gives the geometrical bow, calculated by the formulæ

$$3 \cos^2 \phi = \mu^2 - 1, \quad \sin \phi = \mu \sin \phi', \quad \text{radius} = 4\phi' - 2\phi,$$

from the values of μ for water at 0°C. , quoted by Landolt and Börnstein. The indices for $\text{H}\alpha$, $\text{H}\beta$, $\text{H}\gamma$ are from Wüllner, the other three from Rühlmann. I have drawn the curve on the supposition that the small difference between the results of the two sets is constant. The other curves are separated from this by distances proportional to $\lambda^{\frac{2}{3}}$ and to 3, 5, 6, 7, 10, and 12 respectively, and may serve to represent either the rainbow or any of the supernumeraries. The two dotted vertical lines indicate roughly the boundaries of the bright part of the spectrum. The temperature-effects are trifling and may be disregarded. At 60°F. all the radii are some 4' larger. Below 32°F. the indices of refraction and, consequently, the radii are almost constant.

Nowhere is the superposition of colours perfect. But about $36^\circ 45'$ they may be all contained within $15'$, so that any supernumeraries near that radius must be colourless. At 32° the spread of the colours is nearly as great as in the geometrical bow, and in the reverse order. In practice, however, we cannot expect the same vivid colouring under the most favourable circumstances, as the first supernumerary, for

example, when its maximum is at 32° , must have a breadth of over 5° in homogeneous light (see fig. 2).

We are now in a position to understand the observations better. The most complete measurements are those of (7). Here the mean radius of the dark space between the two bows is $35^\circ 40'$. This is 6° less than the mean radius of the geometrical bow. Assuming this is given by $m=2.50$, the values of m corresponding to the radii observed are as follows:—

	<i>m.</i>
Outside or red of outer bow	0.12
Middle „	0.98
Inside „	2.12
Outside of inner bow	2.89
Inside or red „	3.88

The agreement with fig. 1 is as good as could be expected. Also by fig. 3 the inner bow is small enough to be distinctly coloured. The drops are larger than in the second case of fig. 2. We find indeed for equation (2), taking χ as $6\pi/180$, q as 0.465, m as 2.48, and λ as 0.00056 millim., that their average diameter is 0.041 millim.

In (1) the outer radius is greater than that of the geometrical bow. This finds its explanation in fig. 2.

(2) seems to be a transition stage between a rainbow and an ordinary fog-bow.

(5) By fig. 1 the first supernumerary is much narrower than the main bow.

Taking the radius of (9) as $37^\circ 8'$ we find the average diameter of the drops 0.018 millim.

In (17) the measurements of the inner bow show conclusively that it was the main primary bow, the drops being much the same size as in the second case of fig. 2. So the faint outer bow must have been a modified form of the secondary rainbow. It may be remarked that the effect of the drops being small on the secondary rainbow is similar to the effect on the primary, except that the supernumeraries are outside and the radii are made larger instead of smaller.

It will be observed that the air-temperature in (3), (4), (5), (6), (7), (10), and (18) is below freezing-point; in (5) as low as $15^\circ.7$ F. I have nevertheless assumed throughout that the phenomena are due to drops of water and not to any form of ice. The correctness of this assumption is established by the agreement of observation with Airy's theory, as well as by the identity of the phenomena above freezing-point;

(12), (13). The suggestion that we have to deal with perfect spheres of ice may be put on one side. In the first place, I have never heard of such being observed; and, secondly, if such were to exist for a moment, either evaporation or deposition would soon destroy the perfection of form. Nor do I think it probable that such small drops could be raised much above the temperature of the air by the sun's radiation. Indeed I have often seen the air in Davos, when only a few degrees below freezing-point, filled with floating crystals of ice sparkling in the brilliant sunshine. I am thus led to think that these drops on Ben Nevis were originally formed in air above the freezing-point, and, being free both from jars and from contact with foreign bodies, have been cooled far below 32° F. without congelation. Drops of water suspended in oil of the same density have been cooled by Dufour to -4° F. If this opinion be correct, the drops on striking any object should freeze instantaneously.

I quote the following from an article in 'Nature' (April 9, 1885), by Mr. Omond:—"In addition to the actual fall of snow, hail, &c., there is on Ben Nevis a form of solid precipitation scarcely known on lower ground, but of almost daily occurrence here. In ordinary weather the top of the hill is enveloped in drifting fog, and, when the temperature of the air and ground is below freezing, this fog deposits small crystalline particles of ice on every surface that obstructs its passage. These particles on a wall or large sloping surface... combine to form long feathery crystals; but on a post or similar small body they take a shape more like fir-cones with the point to windward." The deposit only forms on the windward side of each object. Its rate of growth may exceed an inch per hour. As far as I can judge from the above description the deposit is just what might be expected from liquid particles below 32° F., drifting with the wind. If the fog particles were dry ice, how should they stick together to form the feathers? I may suggest further, that in the upward deflexion of the wind by the slopes of the mountain we have an excellent reason for the cooling of the air after the drops were formed.

Hotel Buol, Davos,
April 1890.

LII. *On a Method of Discriminating Real from Accidental Coincidences between the Lines of Different Spectra.* By C. RUNGE, *Professor of Mathematics at the technische Hochschule, Hanover**.

IN the Philosophical Magazine for January 1888 E. F. J. Love gives a method of discriminating real from accidental coincidences between the lines of different spectra. The method is as follows:—The differences between the wave-lengths of the lines compared are arranged in groups, each group containing those observations the errors of which lie within certain narrow limits. The number of observations in each group is then plotted as an ordinate of a curve, the average error of the group being the abscissa. It seems allowable to assume that this curve will have the form of the curve given by the law of error $y = ae^{-c^2x^2}$ in case the coincidences are real and not merely accidental. Any serious divergence from the form of the latter curve will therefore indicate that the coincidences are accidental. So far, I think, one may agree with the author. But he argues further:—If the plotted curve resembles the curve given by the law of error, the coincidences are not accidental. I do not see the necessity to draw this conclusion. On the contrary, I am able to show that for a certain distribution of lines in one spectrum the plotted curve must always resemble the error curve for any lines that one pleases to take as lines of the other spectrum. Let $\lambda_0, \lambda_1, \dots \lambda_n$ be the wave-lengths of any spectrum, λ_0 the smallest and λ_n the largest. What then is the probability that an arbitrary number λ between λ_0 and λ_n does not differ by more than x from the nearest of the wave-lengths $\lambda_0, \lambda_1, \dots \lambda_n$? To find this probability one must add together all the parts between λ_0 and λ_n that differ by not more than x from one of the numbers $\lambda_0, \lambda_1 \dots \lambda_n$. This sum divided by $\lambda_n - \lambda_0$ is equal to the probability in question. Let $d_1, d_2 \dots d_n$ signify the differences of two consecutive wave-lengths in such order that $d_1 \leq d_2 \leq d_3 \dots \leq d_n$, and let d_{v+1} be the first of these quantities, that is not smaller than $2x$, so that $d_v < 2x \leq d_{v+1}$. Then all the intervals $d_1, d_2, \dots d_v$ have to be included in the sum, whilst for each of the intervals $d_{v+1}, d_{v+2}, \dots d_n$ only a part equal to $2x$ has to be added. We find therefore the probability in question

* Communicated by the Author.

equal to

$$\frac{d_1 + d_2 + \dots + d_v + 2(n-v)v}{\lambda_n - \lambda_0}.$$

From this expression one may deduce a simpler one for the probability that the difference between the arbitrary number λ and the nearest of the wave-lengths $\lambda_0, \lambda_1 \dots \lambda_n$ lies between $\frac{d_v}{2}$ and $\frac{d_{v+1}}{2}$. It is

$$\frac{d_1 + d_2 + \dots + d_v + (n-v)d_{v+1}}{\lambda_n - \lambda_0} - \frac{d_1 + d_2 + \dots + d_{v-1} + (n-v+1)d_v}{\lambda_n - \lambda_0}$$

or

$$\frac{(n-v)(d_{v+1} - d_v)}{\lambda_n - \lambda_0}.$$

Let us take $\frac{d_1}{2}, \frac{d_2}{2} \dots \frac{d_n}{2}$ as abscissas, and let us draw a rectangle over the interval $\frac{d_v}{2}$ to $\frac{d_{v+1}}{2}$ with $\frac{d_{v+1} - d_v}{2}$ as base and $2 \frac{n-v}{\lambda_n - \lambda_0}$ as height. Then the area of this rectangle will represent the probability, that the difference of λ from the nearest wave-length lies between $\frac{d_v}{2}$ and $\frac{d_{v+1}}{2}$ (for $v=0$ write $d_0=0$).

Thus we get what we may call a curve of difference analogous to the curve of error. The curve of difference forms the profile of a staircase, the steps of which may be of different height and depth. If n is a large number and the scale of the drawing not too large, the staircase will resemble a smooth curve; and it may be seen from the following application that there are cases where it closely resembles the curve $y = \frac{2c}{\sqrt{\pi}} e^{-c^2 x^2}$, if one is allowed to choose the constant c accordingly.

I have taken as an example the first five ultra-violet bands of the water-spectrum as observed by Liveing and Dewar*. They consist in 598 lines extending from 2268 to 3203.5.

* Phil. Trans. of the Roy. Soc. 1888.

Abcissa.	Ordinate.	Abcissa.	Ordinate.	Abcissa.	Ordinate.
·00 to ·05	1·28	·90 to ·95	·35	1·85 to 1·90	·05
·05 „ ·10	1·28	·95 „ 1·00	·32	1·90 „ 2·00	·04
·10 „ ·15	1·27	1·00 „ 1·05	·28	2·00 „ 2·05	·04
·15 „ ·20	1·26	1·05 „ 1·10	·25	2·05 „ 2·10	·04
·20 „ ·25	1·24	1·10 „ 1·15	·23	2·10 „ 2·15	·03
·25 „ ·30	1·18	1·15 „ 1·20	·20	2·15 „ 2·20	·03
·30 „ ·35	1·10	1·20 „ 1·25	·18	2·20 „ 2·25	·03
·35 „ ·40	1·02	1·25 „ 1·30	·15	2·25 „ 2·30	·02
·40 „ ·45	·96	1·30 „ 1·35	·13	2·30 „ 2·35	·02
·45 „ ·50	·90	1·35 „ 1·40	·11	2·35 „ 2·50	·02
·50 „ ·55	·82	1·40 „ 1·45	·11	2·50 „ 2·65	·02
·55 „ ·60	·74	1·45 „ 1·50	·11	2·65 „ 2·80	·01
·60 „ ·65	·67	1·50 „ 1·55	·09	2·80 „ 3·05	·01
·65 „ ·70	·59	1·55 „ 1·60	·08	3·05 „ 3·35	·01
·70 „ ·75	·57	1·60 „ 1·65	·07	3·35 „ 3·65	·01
·75 „ ·80	·50	1·65 „ 1·75	·06	3·65 „ 3·80	·01
·80 „ ·85	·44	1·75 „ 1·80	·06	3·80 „ 5·70	·00
·85 „ ·90	·39	1·80 „ 1·85	·05	5·70 „ 6·70	·00

In order to compare these values with those given by the law of error, I have for the sake of simplicity interpolated the values of the ordinate for $x=0\cdot1, 0\cdot2$, &c., by taking the mean of the two neighbouring ordinates. The third column contains the ordinates of the curve $y = \frac{2c}{\sqrt{\pi}} e^{-c^2 x^2}$ for $c=1\cdot148$. The table shows the close agreement between the two curves.

Abcissa.	Ordinate curve of difference.	Ordinate curve of error.	Abcissa.	Ordinate curve of difference.	Ordinate curve of error.
·0	1·28	1·30	1·3	·14	·14
·1	1·28	1·28	1·4	·11	·10
·2	1·25	1·23	1·5	·10	·07
·3	1·14	1·15	1·6	·08	·04
·4	·99	1·05	1·7	·06	·03
·5	·86	·93	1·8	·06	·02
·6	·70	·81	1·9	·05	·01
·7	·58	·68	2·0	·04	·01
·8	·47	·56	2·5	·02	·00
·9	·37	·45	3·0	·01	·00
1·0	·30	·35	3·5	·01	·00
1·1	·24	·26	4·0	·00	·00
1·2	·19	·19			

With the spectrum of the water-bands we may now compare any other spectrum we please that lies between the extreme lines of the water-bands. We must expect to find the number

of differences between certain limits equal to the area of our curve of difference between the same limits multiplied by the number of lines of the second spectrum. And if a curve is plotted in the manner indicated by Love, it evidently must resemble the curve given by the law of error, whatever the second spectrum may be. In this case, therefore, the method of Love cannot give us any information whether the coincidences between the lines of the two spectra are real or accidental. But we may derive some information by considering the value of the constant in the formula given by the law of error. Supposing the coincidences to be real ones, the differences between the lines compared must be distributed

according to the formula $y = \frac{2c}{\sqrt{\pi}} e^{-c^2 x^2}$. If now we can make

an estimate of c and find it considerably larger than 1.148, the distribution of differences ought to show a divergence from the distribution given above. If the divergence is not shown, the coincidences must be accidental. Only when c is not found considerably larger than 1.148 we are left without an answer. The distribution of differences would then be the one given above, and would afford no reason to think the coincidences real ones.

The most important verification of A. Grünwald's far-reaching speculations on the composition of the elements he believes to be afforded by the agreement between the wave-lengths of the lines in the spectrum of water, as deduced by him from those of the hydrogen spectrum, and their values as obtained by observation. But I find that the distribution of differences is in perfect accordance with the one expected for an equal number of wave-lengths chosen at random. To show this more clearly, I have taken the mantissas of $\log \sin$ from $9^\circ 43'$ to $12^\circ 4'$, and of $\log \tan$ from $19^\circ 20'$ to $19^\circ 38'$ for each minute abbreviated to five figures. These numbers lie between the extreme wave-lengths of the water-bands. The distribution of differences between each of these numbers and the nearest wave-length of the water-spectrum does not show any serious divergence from the distribution corresponding to the wave-lengths calculated according to Grünwald's theory by multiplying the wave-lengths of hydrogen by $\frac{1}{2}$ *.

The first column of the following table contains the limits

* I have taken Hasselberg's measurements, *Mém. de l'Acad. de St. Pétersbourg*, 1882, as Grünwald has preferred these to the more complete measurements of 1883. I have abbreviated the halves to five figures, adding a unity to the fifth figure when it was even.

of the differences, the second gives the expected number of differences within these limits, the third the observed number corresponding to the wave-lengths calculated from hydrogen, the fourth the observed number corresponding to the said mantissas of log sin and log tan.

Limits of differences.	Expected numbers.	Observed numbers.		Limits of differences.	Expected numbers.	Observed numbers.	
·00 to ·05	10·4	12	6	2·05 to 2·15	0·6	2	1
·05 " ·15	20·6	16	26	2·15 " 2·25	0·5		
·15 " ·25	20·2	19	16	2·25 " 2·35	0·4		
·25 " ·35	18·4	21	16	2·35 " 2·45	0·9		
·35 " ·45	16·0	19	15	2·45 " 2·55		1	
·45 " ·55	13·8	16	16	2·55 " 2·65			
·55 " ·65	11·3	11	12	2·65 " 2·75	0·7	1	
·65 " ·75	9·3	8	9	2·75 " 2·85			
·75 " ·85	7·5	7	11	2·85 " 2·95			
·85 " ·95	5·9	5	12	2·95 " 3·05	0·6	1	
·95 " 1·05	4·9	6	1	3·05 " 3·15		1	1
1·05 " 1·15	3·8	1	5	3·15 " 3·25			
1·15 " 1·25	3·1	...	2	3·25 " 3·35	0·4	1	
1·25 " 1·35	2·2	3	3	3·35 " 3·45			
1·35 " 1·45	1·8	1	2	3·45 " 3·55			
1·45 " 1·55	1·6	3	2	3·55 " 3·65	0·4		
1·55 " 1·65	1·1	...		3·65 " 3·75			
1·65 " 1·75	1·0	...	1	3·75 " 3·85			
1·75 " 1·85	0·9	2	2	3·85 " 5·25	1·0	1	1
1·85 " 1·95	0·7	...		5·25 " 6·75	0·7	1	
1·95 " 2·05	0·7	2	1				

As the distribution of the differences corresponding to the wave-lengths calculated from hydrogen is in accordance with the expected distribution, it follows either that the coincidences are accidental or that their probable error is not smaller than the one corresponding to $c=1\cdot148$. The probable error for $c=1\cdot148$ is 0·42. That is to say, $0\cdot42 \times 10^{-7}$ millim., as 10^{-7} millim. is the unit of the wave-lengths. It seems to me not impossible that the probable error of the difference between Liveing and Dewar's measurements and the halves of Hasselberg's is as much as 0·42. One cannot therefore, without more exact measurements, safely infer that Grünwald's coincidences are accidental. However, one can say that the distribution of differences gives no more reason to believe the coincidences real than to believe in a connexion between the mantissas of log sin and the spectrum of water.

LIII. *On Texture in Media, and on the Non-existence of Density in the Elemental Æther.* By G. JOHNSTONE STONEY, a Vice-President of the Royal Dublin Society, M.A., D.Sc., F.R.S.*

IN the investigations of ordinary dynamics—the dynamics of secondary† motion—integrations have to be extended throughout the bodies with which we are dealing, or over their surfaces. Now whenever we employ this operation, assumptions are tacitly made which do not accord with what exists in real objective nature.

Suppose that the problem is to obtain the pressure of water against a sluice; to ascertain the amount and distribution of the pressure, we integrate over the surface between the water and the sluice, and in doing so assume:—

- (1) That the boundary is a surface; and
- (2) That the elements into which we conceive this surface

* Read before the Royal Dublin Society, February 19, 1890, and reprinted by permission from a proof of the paper in the Scientific Proceedings of the Society.

† In the computations of ordinary dynamics, we conceive the portion of space occupied by the body with which we are dealing to be divided into elements of volume (the $dx dy dz$'s), which elements of volume we regard as movable. Each of these we multiply by a coefficient called the density, and call the product the element of mass ($dm = \rho . dx dy dz$). These elements of mass we picture to ourselves as acting on one another, or as being acted upon by external forces; and from the laws of these actions we endeavour to deduce the motion of the element of volume, carrying its contents with it, and in some cases changing its form or volume.

In this process we take no notice of any motions which may be going on within the element of volume, except so far as that some imperfect account may perhaps be indirectly taken of them when we multiply the element of volume by a density. Nevertheless, in all the real cases that occur in nature, there are, as a matter of fact, *very active* motions of various kinds going on within the element of volume: motions of the molecules which it contains, and still more deep-seated motions within the portion of the element of volume occupied by those molecules, or in the interspaces between them.

Accordingly the motions with which we deal in our ordinary dynamical investigations are merely drifting motions—the drifting about of elements of volume, within each of which, as events really occur in nature, there are elaborate subsidiary motions going on. Now, *secondary motion* is to be defined as the motion which consists in the drifting about, with or without changes of size and form, of elements of volume *within each of which there are subsidiary motions*.

If the subsidiary motions consist exclusively of irrotational motions in an incompressible and perfectly fluid medium, they cannot contribute to the density by which the element of volume in which they occur is to be multiplied. It is, however, otherwise if there are any rotational motions present.

divided for the purposes of the integration may be made as small as we please without ceasing to be subjected to the law in heavy liquids of pressure proportional to the depth below the upper surface of the water, plus that due to the superincumbent atmosphere.

Both these assumptions continue approximately true when the elements into which we suppose the surface divided are diminished till they are as small as, or even a good deal smaller than, the smallest speck that can be distinguished with the most powerful microscope; but they utterly break down if we suppose the subdivision carried so much further as to reach or even approach the scale of molecular magnitudes. If, for instance, the elements into which we suppose the surface divided were reduced to a square tenth-metret* in size, a patch of surface which is the millionth part of the utmost a microscopist can see, we should have got well within the range† of molecular differences. The boundary between the water and sluice would cease to be a surface: it would be the continually shifting boundary between molecules on both sides in energetic motion, acting individually on each other in their own special ways; which happen to be such that when immense numbers of these individual operations are lumped together they produce approximately, as the outcome of all that is going on, that law of pressure proportional to depth with which we are familiar.

Thus, what we regard as a physical property of the medium—in this case the law of pressure in a heavy liquid—is in reality a statement of what is the drift of a vast number of individual events, grouped together by a kind of statistical process. This we may briefly describe by saying that the dynamical properties of the medium are due to its *texture*,

* The decimetre is the first of the metrets (*i. e.* decimal subdivisions of the metre), the centimetre is the second, the millimetre is the third. The tenth-metret is the tenth of this series. It is a metre divided by 10^{10} . The waves of visible light have lengths varying from 3900 to 7600 of these tenth-metrets.

† According to Professor Loschmidt, who first published an estimate of the interval within which the centres of two molecules must approach to act sensibly on one another, this interval is about a ninth-metret (Proceedings of the Mathematical Section of the Academy of Vienna, Oct. 1865, p. 404). The mean of such intervals may, perhaps with more probability, be taken as lying nearer to the tenth-metret. It is very improbable that it is as small as the eleventh-metret. In the present paper I assume it to be about the tenth-metret. If, however, it lies nearer the ninth-metret, though we shall have to change almost all the numbers of the computation in the text, we shall arrive at a conclusion not materially differing from that on p. 472 below.

meaning by the texture of a medium whatever is going on in it at close quarters.

It is the same with the other recognized physical properties of media, such as what are called gaseous laws—the laws connecting the density, temperature, and pressure of gases, the laws of their diffusion, the law of viscosity, and so on. Similarly with the properties of solid bodies: all are the outcome of vast numbers of very diverse individual events that occur between or within the molecules of the bodies, or between them and the luminiferous æther.

In order to penetrate to this world of individual actions, we must not only descend to magnitudes that are comparable to the intervals at which the centres of molecules are spaced from one another, but we must also consider periods of time that are not too vast in reference to the motions that go on among them. A second of time is “out of all whooping” too long*; but a period which is definite and of suitable brevity is that for which I have elsewhere proposed the symbol τ , viz. the time that light takes to advance one millimetre *in vacuo*. The velocity of light being 30 quadrants per second, and the quadrant (the length of a meridian from the Earth’s equator to the pole) being 10^{10} millimetres, we find that

$$\tau = \frac{1}{3} \cdot \frac{\text{one second}}{10^{11}},$$

i. e. it is one third of the eleventh† of a second of time. In this fragment of time, visible light makes from 1300 to 2600

* See the Philosophical Magazine for August 1868, p. 140, footnote. Readers of the paper here referred to are requested to change the square of 16 in the second paragraph into the square root of 16. In that paper (p. 141) I estimated the number of molecules in a cubic millimetre of a gas, at atmospheric temperatures and pressures, as about a uno-eighteen (10^{18}), without being aware that a similar estimate had been obtained for solids and liquids by Professor Loschmidt in 1865 (Proceedings of the Mathematical Section of the Academy of Vienna for October 1865, p. 405). In March 1870 Sir William Thomson, doubtless also without knowing of what had been done before, published a paper in ‘Nature’ on the “size of atoms,” and arrives at substantially the same estimates as Professor Loschmidt and myself.

The earliest determination of a molecular magnitude, so far as I am aware, was that made by Professor Clerk Maxwell of the mean length of the “free paths” of the molecules of certain gases in their excursions between their encounters. See Philosophical Magazine for January 1860, p. 32, and for July 1860, p. 31. See also Philosophical Transactions for 1866, p. 258.

† The eleventheth means a unit in the eleventh place of decimals. It accordingly is a name for the fraction 0·000, 000, 000, 01, or $\frac{1}{10^{11}}$.

vibrations according to its colour, so that the mean frequency of vibration of light is about 2000 vibrations during each τ^* . [This mean is the actual frequency of that green ray whose wave-length in *vacuo* is 5000 tenth-metres.]

We may now get some insight into the physical events that occur in the world into which we have passed. The pressure of air in this room against the walls is, according to the kinetic theory of gases, due to the walls being bombarded by molecules of air as they fly about like missiles. It is an elementary proposition† in the kinetic theory of gases that the momentum communicated to the wall is substantially the same when, as actually happens, the molecules frequently encounter one another throughout the room, as it would be if the aerial missiles could be divided into three equal squadrons, one of which should travel uninterruptedly up and down between the floor and ceiling, another squadron travelling horizontally from side to side, and the third squadron from end to end of the room; and all moving with a velocity whose square is the mean of the squares of all the actual velocities of molecules in the room. This "velocity of mean square," as it has been called, depends on the molecular mass and on the temperature of the gas; and in the case of the air in this room it is about 500 metres per second‡. Let us then suppose the wall to be struck by one third of the molecules in this room, rushing backwards and forwards between it and the opposite wall at this pace; and let us endeavour to form an estimate of how often one of the superficial molecules of the wall will be subjected to an encounter.

The number of molecules in a cubic millimetre of the air is known to be about a uno-eighteen (10^{18})§; and there are of course 500,000 times this number in a column 500 metres long and a square millimetre in section, *i. e.* there are 5 uno-twenty-threes in this column. One third of all the molecules in the column are the squadron that we are to regard as travelling lengthwise, half of these advancing towards one end and the other half retiring from it. It thus appears that the number of molecules within the column to be taken as travelling at any instant *towards* one end is $\frac{5}{6} \cdot 20^{23}$. This accord-

* See British Association Tables of Oscillation-frequency, B. A. Report for 1878, p. 40.

† See Maxwell's 'Heat.'

‡ Phil. Mag. 1857, xiv. p. 124; or Maxwell's 'Heat.'

§ See footnote *, p. 469. The uno-eighteen means the number represented by 1 with eighteen cyphers after it. It accordingly is the same as 10^{18} .

ingly is the number that will strike against a square millimetre of the wall in one second. Now the time τ being, as we have found, $\frac{1}{3}$ of an eleventheth of a second ($\frac{1}{3} \times \frac{1}{10^{11}}$ of a second), it follows that $\frac{5}{18} \times 10^{12}$ is the number of downright blows that would be delivered by these molecules upon one square millimetre of the wall in the time τ .

This is on the supposition that the molecules are divided into three squadrons. They are not so divided in reality, and accordingly all the strokes delivered against the square millimetre of the wall are not downright blows, but are many of them oblique. An easy computation shows that this will increase the number of blows in the ratio of 3 to 2* ; so that

* If N be the number of downright blows delivered on a surface s in the time T , and if α be the momentum communicated by each blow, then the pressure they will occasion

$$= \frac{N\alpha}{sT} \dots \dots \dots (1)$$

If, on the other hand, the blows arrive from all quarters indifferently, and if dn' be the number reaching s from inclinations between θ and $\theta + d\theta$, θ being measured from the normal, then will

$$dn' = k \cdot s \cos \theta \cdot 2\pi d \cos \theta, \dots \dots \dots (2)$$

where k is such that $k \cdot d\sigma$ is the number of blows coming from directions lying within an element $d\sigma$ of solid angle, that would be received in the time T , by a unit of surface presented perpendicularly to the shower.

These dn' molecules communicate to s a momentum

$$= \alpha \cos \theta \cdot 2\pi k s \cos \theta d \cos \theta.$$

Therefore the whole momentum communicated in this way from all inclinations

$$= 2\pi k s \alpha \int_0^1 \cos^2 \theta d \cos \theta = \frac{2}{3} \pi k s \alpha ;$$

and the pressure thus caused

$$= \frac{2}{3} \frac{\pi k \alpha}{T} \dots \dots \dots (3)$$

This is to be equal to the pressure produced by N downright blows ; whence, equating (1) and (3),

$$N = \frac{2}{3} \pi s k \alpha \dots \dots \dots (4)$$

Again, N' , the number of blows that reach s , when molecules fly in all directions,

$$= \int dn' = 2\pi s k \cdot \int_0^1 \cos \theta d \cos \theta ;$$

whence

$$N' = \pi s k \dots \dots \dots (5)$$

Comparing (4) and (5), we find that

$$\frac{N'}{N} = \frac{3}{2}$$

as in the text.

the real number of blows delivered upon the square millimetre is about $\frac{5}{12} \times 10^{12}$.

Next consider the distance within which the centres of two molecules, one a molecule of the air and the other a molecule of the wall, must approach in order that they may sensibly act on one another. A circular disk, with this distance as radius, may be considered as a target towards which the centre of a molecule of the air must be directed in order that this particular molecule of the wall may be reached. Now the distance within which the centres of the molecules must approach lies more probably in the neighbourhood of a tenth-metret than in the neighbourhood of either a ninth-metret or an eleventh-metret*. Let us for the purpose of an estimate assume that it is a tenth-metret. The size of the target, supposed flat, will then be about three square tenth-metrets.

This is 3 fourteenthths of a square millimetre ($3 \times \frac{1}{10^{11}}$ of a square millimetre). Accordingly the number of encounters this molecule will receive in the time τ will be approximately

$\frac{5}{12} \cdot 10^{12} \times 3 \cdot \frac{1}{10^{14}} = \frac{1}{80}$. This is on the supposition that the target to be struck is a disk, whereas it is in reality a sphere. This will double† the number of blows it will be subjected to in the time τ ; whence, finally, we may take this number to

be about $\frac{1}{40}$: in other words, this molecule of the wall is struck on the average at intervals of about 40 times τ . If the colour of the wall be green, the molecular motions which occasion this colour are repeated in the molecule 2000 each τ , and therefore something like 80,000 in the intervals between the shots to which the molecule is subjected by the aerial artillery. This serves to explain why the incessant bombardment by the

* See footnote † (p. 468).

† N' , the number of blows that reach a circular disk of radius a , is, according to equation (5) of footnote * (p. 471),

$$N' = \pi^2 a^2 k. \quad \dots \dots \dots (6)$$

Again, proceeding as in equation (2) of footnote * (p. 471), we find that the number N'' which would reach a sphere with radius a ,

$$\begin{aligned} N'' &= \int_0^1 k \cdot \pi a^2 \cdot 2\pi d \cos \theta, \\ &= 2\pi^2 a^2 k. \quad \dots \dots \dots (7) \end{aligned}$$

Comparing (6) and (7), we find that

$$N'' = 2N'.$$

air does not alter the colour of the wall. Between the encounters long intervals elapse: intervals so long compared with the motions of light, that any small* disturbance in the periodic time which may be caused by the encounter probably lasts for but a very trivial part of the long intervals of respite.

Thus in both liquids and gases, what are called the dynamical properties of the medium do not exist when we come to close quarters; and, accordingly, investigations based on these dynamical properties, and carried out by integrations, will yield results that are valuable only when the integration $(\iiint \phi(x, y, z) dx dy dz)$ furnishes a result nearly identical with that which would be furnished by a summation $(\sum \phi(x, y, z) \Delta x \Delta y \Delta z)$, where each of the blocks $\Delta x \Delta y \Delta z$ is sufficiently large to include an enormous number of the individual operations that are in reality what actually go on in the medium.

We come upon the same result when we make a similar inquiry with regard to solids. But I forbear going into numerical details in this branch of our subject until I can publish investigations on which I was engaged some years ago, by which it appears that the form and dynamical properties of many crystals can be connected with their chemical constitution. When this subject is gone into, it becomes plain that the dynamical properties of solids also, such as their power of propagating shearing-stresses, are, like those of liquids and gases, due to events of an utterly different kind that occur between parts so close, and in periods of time so brief, that enormous shoals of these events occur in a very small fraction of a second, within elements of volume many times smaller than the most tiny speck the microscope can show. Accordingly, what we regard as dynamical properties

* Probably but small; since the periodic time seems to depend much more on the relation which subsists (and acts without intermission) between ponderable matter and the luminiferous æther, than upon the occasional events which occur in the grappling of molecules with one another.

This view is borne out by observations made by the author on the absorption-spectrum of the vapour of chlorochromic anhydride (CrO_2Cl_2), the lines of which were found to have sensibly the same appearance whether air was or was not present with the vapour. It was expected that the spectrum might exhibit an appreciable difference in these two cases, since when air is present the molecules of the vapour are subjected to a largely multiplied number of encounters—notwithstanding which no alteration in the appearance of the lines of the spectrum could be detected.

For an account of the *very* remarkable spectrum of this vapour, see a paper by Professor Emerson Reynolds, F.R.S., and the Author, in the *Philosophical Magazine* for July 1871, p. 41.

of solids, such as their power of propagating tensile, compressive, shearing, and twisting stresses, are an outcome of what I have called the *texture* of the medium; and only appear between blocks so large that, in considering the effect of one of these large blocks upon its neighbours, we need only take account of the general outcome that emerges when vast numbers of the individual events that are actually going on are combined, and *their general drift* obtained by a statistical method.

It is especially instructive in this connexion to consider the problems of that branch of dynamics which is called Rigid Dynamics—such as the investigation of the motions of a top, or hoop, or of the precessional motion of the Earth. In these inquiries the integral calculus is employed. But the integrations are all such that the calculated motions of such bodies would come out almost precisely the same, whether the absolute limit, as furnished by the integrals, be taken, or a summation for which the volume of the rigid body is regarded as divided into blocks as large as the smallest specks visible in the microscope. It is desirable, however, that we should bear in mind that *there is the widest difference between the physical assumptions underlying these two methods of procedure.*

If we proceed by integration, it is tacitly assumed that the stresses characteristic of a solid body prevail between elements of the volume *however small*, and differ, according to the law laid down as the law prevailing in the medium, at situations in the body *however near*. This is not true.

On the other hand, if we proceed by summation, it is assumed that the forces acting on each little block are distributed equally and without any variation of direction to the several equal portions into which its little mass may be conceived to be divided, however minute this subdivision may be. If this were the case, *the internal stresses of a rigid body would be powerless to induce rotation in any one of these blocks, or to alter any rotation that may have pre-existed in it.* Accordingly each of these blocks would not *rotate* round the instantaneous axis: it would merely revolve round it*. These, which are the real physical meanings of the assumptions made in the two cases respectively, are specially instructive.

About fifty years ago Professor MacCullagh announced his great discovery that the phenomena of light could be accounted for, if we suppose light to be an undulation in an *incompress-*

* The proper inference from this is that our equations have only taken into account a part of the forces that are really acting: and this is true.

sible medium of uniform density, endowed with those dynamical properties which are embodied in his fundamental equations. These properties are not very unlike the properties attributed to an ordinary solid body; and the question now arises, whether these properties (or whatever are the real dynamical properties of the medium in which are propagated light, radiant heat, and other waves of electromagnetic stress) are fundamental properties of the medium; or whether, like the properties of solids, liquids, or gases, they *are the outcome of events of a wholly different character* happening at intervals so short that the elements of volume (the $dx\,dy\,dz$'s of MacCullagh's formulæ) contain *vast* numbers of them. Now the dynamical properties of the luminiferous medium—whether we use MacCullagh's or Cauchy's fundamental equations—sufficiently resemble those of media which we know to be “textured,” to make the latter supposition the more probable, after what we have found to be the real nature of solid, liquid, and gaseous media. And this probability is very much strengthened by the discovery made by Helmholtz about a quarter of a century ago, of the persistence and dynamical behaviour of vortex-rings and other vortex filaments in a *perfect* incompressible fluid, and by the investigations to which this discovery has led.

One result of these investigations has been to suggest to Sir William Thomson that the chemical atoms of which ponderable matter consists may be simply vortex tangles in such a medium; and to suggest to Professor FitzGerald that the luminiferous æther may be a medium of this kind permeated by straight vortex filaments in all directions. Investigations are being actively pushed forward with a view to ascertaining how far these suppositions can be corroborated. Other hypotheses which may be classed with these have been advanced by Professor Hicks and others, but I select Professor FitzGerald's and Sir William Thomson's, both because they seem, in our present imperfect state of information, the best of their class, and in order to give definiteness to what further I have to say.

Let us then imagine this room to be permeated by three systems of wires. Let the first be a set of vertical wires from the ceiling to the floor in rows parallel to the walls, and at intervals from one another of one inch. Let a similar system cross the room from side to side, passing midway between the wires of the first set: and let a third system of wires run from end to end of the room threading their way along the middle of the clear passages that lie between the wires of the other two systems. Let these wires represent straight vortex filaments in a uniform incompressible medium devoid of

any stress that resists change of form, and let the alternate vortex filaments of each row rotate in the same direction, while the intermediate ones rotate in the opposite direction, but let the vortex filaments be in other respects similar.

Such would be the simplest case of a medium of the kind that Professor FitzGerald has conceived*. Let us next imagine the whole space within the room to be divided into large blocks of a cubic yard in size. One of these blocks will include a great number of the vortex filaments, and all the large blocks will closely resemble one another; insomuch that if an undulation consisting of shallow waves each a quarter of a mile long were to traverse the medium, the blocks would appear to act on one another in a certain definite way. This corresponds to the way in which Professor MacCullagh's elements of volume, his $dx dy dz$'s, are in his formulæ assumed to act, and the waves correspond to his waves of light. But if the whole space were divided into much smaller blocks, suppose into cubes of half an inch, great differences would be found to prevail between these small blocks, and equally great differences in the way they act on one another; and the difference would become more striking if the subdivision were carried so far as to render the blocks small in comparison with the thickness of the wires that represent vortex filaments.

If, now, we further conceive small vortex tangles travelling about in this medium, the long vortex filaments opening to let them pass, and acting in front, sideways, and behind upon them in such a way as to urge them equally forwards and backwards, so long as their journey is along a *straight* path with *uniform* speed—we shall have a first sketch of what constitutes ponderable matter and the luminiferous æther, according to these speculations.

The particular hypotheses which are here described may perhaps not have quite hit the mark; but, though we have as yet only a glimmering of this great subject, it is pretty certain that either these hypotheses, or something like them, are the true ultimate account of material Nature.

We must, therefore, carefully distinguish between the elemental and the luminiferous æthers. The elemental æther, until motions create differences in it, is *absolutely* alike and undistinguishable in *all* its parts; and in the mathematical investigation of motions in it, wherever in any of the equations of dynamics an element of mass appears, we must

* 'Nature,' May 1889, xl. p. 32.

write everywhere the element of volume instead. It is itself the integral of these elements of volume; in other words, it is space under a new aspect. In the geometrical way of conceiving space, the parts into which it may be conceived to be divided are thought of as they would be if at rest relatively to one another. In the kinematical way of conceiving space, *which alone is in accordance with what objectively exists*, we are to recognize that each portion of volume is pervaded by the motions that actually subsist within it, and that it can travel about carrying those motions with it. In fact the volume occupied by a block of iron differs from an equal volume occupied by air, *only* by the motions that are going on within the one volume being different from those that pervade the other. In every other respect they are as exactly alike as one stationary portion of space is to another. One such portion of space is not another; but it is *exactly* like it; and *there is no limit* to this resemblance however small the portions compared may be. There is no "texture" until there is motion.

On the other hand, when, in investigating the motions of ponderable matter, we have occasion to conceive the bodies we are dealing with divided into small portions, it is only *if we stop short* in our division so that the blocks we form do not fall below a certain size, that we are justified in treating them as resembling one another. When we thus stop short, the blocks are in reality accumulations of more minute internal motions; and if we do not stop short, but carry the division sufficiently far, we shall come down upon the individual motions themselves, between which of course the most marked differences would be found.

It appears to be the same in regard to the luminiferous æther. It is only when we do not subdivide too far, that we are justified in speaking of the blocks as resembling one another. The luminiferous æther seems to be a textured medium like ponderable matter. But in the elemental æther—in space itself regarded as movable—there are no such limits. Its portions, however small, resemble one another with mathematical exactness*: except so far as there may be different motions prevailing within those portions.

* Empty coreless vortices involve the hypothesis of a medium that is discontinuous and has boundaries; or else (in the case of some coreless vortices) of a medium which obeys two laws of motion, one for the part of the medium that is interned on one side of a closed vortex sheet, and another for the rest of the medium. Now it seems very improbable that the objectively existing elemental æther—space under its kinematical

It thus appears that *the distinction* between different parts, which is implied by the term density, *does not exist** in the elemental æther, and that in it the element of volume *is* the element of mass. There is, accordingly, no such physical quantity as density in the dynamics of the ultimate motions of the elemental æther. It is only when accumulations of these primary motions are lumped together, and where what we are investigating is merely *the drifting about* of these accumulations—it is only in this branch of dynamics that we find the need and the advantage of the conception of density as *a substitute for having to take separately into consideration some of the motions that are really going on*. In fact, if any such hypothesis as Sir William Thomson's is true, the density of a lump of iron, *i. e.* the coefficient by which the elements of its volume have to be multiplied in order to get their masses, is nothing but *a mere function of the primary or elemental motions prevailing in that portion of space*†, and which alone make that portion of space differ from one in which other elemental motions are going on.

aspect—is of either of these kinds; and accordingly it is improbable that empty coreless vortices are any part of real Nature. This is a kind of objection which may raise an improbability, even a great improbability; but we should be rash to rely on it as finally decisive, for the reality of things is not limited by our way of conceiving them.

The objection, such as it is, would not lie against the presence in nature of coreless vortices lined with a vortex sheet and filled in with a part of the medium devoid of rotational motion; but such vortices would in some respects behave differently from empty coreless vortices.

* This conclusion is confirmed by an important ontological proposition which is susceptible of demonstration, *viz.* that nothing that we suppose to exist in nature can be “real,” unless *it is a syntheton of perceptions* actual, potential, or conceivable. Thus, motions and space relations may be “real,” for they are such syntheta; but a “thing to move” is not real *except* in those cases in which the motion we are considering is the drifting motion of volumes within which subsidiary motions prevail. In such cases the subsidiary motions are often thought of, and may, perhaps without objection, be spoken of as a thing that moves.

† That is, on the supposition that the luminiferous æther is of uniform texture throughout its whole extent, as seems to be the case. If, however, the fact be otherwise, we must regard the density of the iron as a function both of the elemental motions pervading its volume and of the elemental motions in the *adjoining* part of the luminiferous æther. The density of the iron would then depend on its situation in the material universe.

LIV. *On the Theory of Dropping Electrodes.*—*Reply to*
Mr. Brown. By Prof. W. OSTWALD*.

IN the April number of the Philosophical Magazine, Mr. Brown raises objection to a remark, which I made in the *Zeitschr. f. ph. Ch.* iv. pp. 577, 578, about his supposed disproof of v. Helmholtz's Theory of Dropping Electrodes. I must regret not having expressed myself clearly enough in that remark, as Mr. Brown has not considered its essential part at all in his note.

Mr. Brown ascribes to v. Helmholtz the opinion that the cause of the galvanic current observed when a mass of mercury dropping in an electrolyte is connected by means of a galvanometer with the mercury collecting at the bottom of the vessel, is the "charges carried down by the drops." I do not know on what passage of Helmholtz's writings Mr. Brown supports this statement; any such is unknown to me. Helmholtz's assumption is, that every drop on its formation becomes covered with an electrical *double layer* similar to the charge of a Leyden jar. This double layer contains positive and negative electricity in equal quantities; its motion cannot therefore give rise to anything that is similar to a galvanic current. From this it follows, conversely, that the galvanic currents produced in this way have no connexion whatever with the *motions* of the drops.

Such a connexion, however, exists with the *formation* and the *destruction* of the drops. Every drop that is produced takes positive electricity from the mercury, and negative from the electrolyte, in order to form its double layer. On the union of the drop with the mass of mercury lying at the bottom, the positive electricity goes over to the latter while the negative electricity remains in the electrolyte, and moves, in case the process continues, to the point of formation of the drops, to produce there new double layers. This latter movement is of course dependent on the resistance of the electrolyte, and Mr. Brown's observation therefore is not, as he believes, in contradiction, but in complete agreement with the theory of Helmholtz.

Against this, Mr. Brown objects that currents are also obtained if the dropping mercury is connected with a secondary mercury electrode which receives no drops. It seemed to me unnecessary to develop the above-given explanation also for this case, since every one who understands that can also here apply it. On Mr. Brown's account I will, however, again

* Communicated by the Author.

expressly state, that also in this case double layers are formed on the drops, whose negative electricity comes from the electrolyte. The supply of this electricity depends therefore on the conductivity of the electrolyte. The process can, however, no longer be a lasting one, because the secondary electrode is immediately polarized. Mr. Brown can easily convince himself (if he has not already noticed it), that the current produced under such circumstances is much weaker than the one earlier mentioned, and that it becomes continually weaker owing to the polarization, while the other current can be kept for days at its original strength.

Finally, it follows from the theory of v. Helmholtz, that a diminishing current of opposite direction must be obtained if the secondary electrode is connected, not with the dropping mercury, but with that collecting on the bottom of the vessel. This current can also easily be observed. According to Mr. Brown's ideas, if I have correctly understood them, in this case no current whatever could be produced.

Brüder Strasse, Leipzie.

LV. *On the Electrical and Chemical Properties of Stannic Chloride; together with the Bearing of the Results therein obtained on the Problems of Electrolytic Conduction and Chemical Action.*—Part I. *Experimental Observations.* Part II. *Theoretical Considerations.* By WARD COLDRIDGE, B.A., *Scholar of Emmanuel College, Cambridge.*

[Concluded from p. 394.]

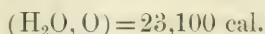
PART II.—THEORETICAL CONSIDERATIONS.

THE first problem that presses forward for consideration is that involved in the nonconductivity of stannic chloride. It is a truism to write that its insulating-power is a function of its constitution; but it has hitherto been difficult, from the lack of experimental observations, to advance beyond that truism. The fact is that a column of stannic chloride, some three to four centimetres in length with a cross section of one to two square centimetres, has a resistance the lower limit of which is certainly not less than 1600 megohms. This phenomenon is not an isolated one. Other pure liquids—water, hydrochloric acid, hydrofluoric acid—are also nonconductors, but liquid hydrocyanic acid is said to be an electrolyte; and the fused salts, of which the silver halogen compounds may be taken as typical, easily electrolyse. Wherein, then, do these liquids which are nonelectrolytes differ from those which are electrolytes? In order to progress towards a solution of this

question a review will now be made :—of the chemical characteristics, as far as they are pertinent, of those compounds ; of the possible influence of their physical aggregation ; and, lastly, of the conditions under which the power of electrolysis can be developed.

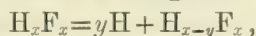
To take the liquids *seriatim* :—

Water is characterized by its stability and by its large heat of formation. If it could be directly oxidized to hydrogen peroxide, the change would involve a large absorption of energy,



Thus it is not possible for pure water to become nonhomogeneous through the formation of any peroxide : the only other way in which water could become chemically nonhomogeneous, save through the formation of molecular aggregates of varying complexity, would be by its dissociation in part into hydrogen and oxygen atoms ; but this is a most remote speculative chance and a practical impossibility.

Hydrofluoric Acid is the only compound of hydrogen and fluorine. There is neither a perfluoride (HF_x) nor a subfluoride (H_xF). Moissan examined the product of the electrolysis of liquid hydrofluoric acid, rendered a conductor by the presence of dissolved potassium hydrogen fluoride, and found no evidence of such a change as

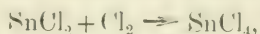


and established that the ions, as liberated, are simply hydrogen and fluorine.

Hydrochloric Acid is the only compound of hydrogen and chlorine. I think that no one has endeavoured to perform with liquid hydrochloric acid experiments analogous to those of Moissan's for the sake of their electrolytic importance.

Stannic Chloride in the vaporized condition can exist perfectly as a collection of like unit particles, molecules SnCl_4

There is a lower compound, stannous chloride : but the forward change,



occurs with the utmost readiness. A strong presumption therefore exists against the possibility of the reverse dissociation, except at high temperatures ; and there is no evidence in support of such an hypothesis.

Thus, then, water, hydrofluoric acid, hydrochloric acid, stannic chloride, agree in their chemical homogeneity.

Whilst there is the closest resemblance between the above

nonconducting liquid acids and the conducting liquid hydrocyanic acid, in point of their physical properties, it may yet be possible to distinguish it chemically: at least it is worthy of note that

$$(H, C, N) = -28,400,$$

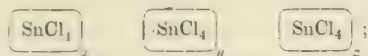
for such a large endothermic formation is suggestive of a tendency towards instability.

The observations of Bleekrode and De La Rue (*Proc. Roy. Soc.* xxv. p. 323), showing its power of electrolysing, are worthy of confirmation, provided all possible precautions be taken to ensure the use of an absolutely anhydrous specimen.

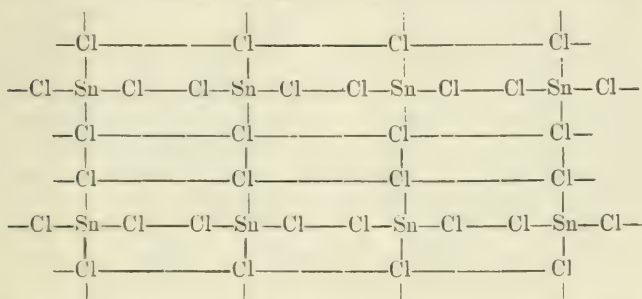
In considering the phenomena presented by the fused salts, it is necessary to recall the warning given by Prof. Armstrong as to the scantiness of accurate data at the command of the inquirer into the properties of fused *pure* substances. Having noted this warning, a statement made by Faraday is very apposite. In the first volume of his '*Experimental Researches in Electricity*,' § 690, when he is discussing the results he had obtained with fused antimony trichloride, he suggests that the conductivity he had observed "might be due perhaps to a true protochloride consisting of single proportionals ($SbCl$)."¹ In a word, Faraday surmised that the fused compound was not quite homogeneous. A similar suggestion may be advanced: that silver chloride, silver iodide, selected as two of the best examples of Faraday's law of Liquid-Conduction, are not homogeneous compounds in the fused state. Photo-salts—whether they be definite compounds or mixtures is of no import—exist and are characterized by the extreme facility of their formation. Probably with more accurate information at command it will be possible to advance, in explanation of the electrolytic conduction of fused substances, this view of the imperfect homogeneity, itself supported by separate and nonelectrical considerations; and to establish as an expression of a complete uniformity that no homogeneous liquid is an electrolyte: electrolisability involves an antecedent condition of heterogeneity.

But in such a statement as that no homogeneous liquid is an electrolyte it is necessary to accurately determine the significance of the word "homogeneous." Without hesitation, for example, pure liquid stannic chloride would be spoken of as homogeneous. The statement would be accurate if the whole of the stannic chloride were composed of precisely similar unit molecules. But a view has been expounded in a profound paper by Prof. Armstrong, "*On Electrolytic Conduction in relation to Molecular Composition; Valency and the Nature*

of Chemical Change ; being an attempt to apply a Theory of Residual Affinity" (Proc. Roy. Soc. 1886, p. 268), that stannic chloride is not thus simply constituted, but that a condition of more complex aggregation is attained of which the particles could be represented thus :—

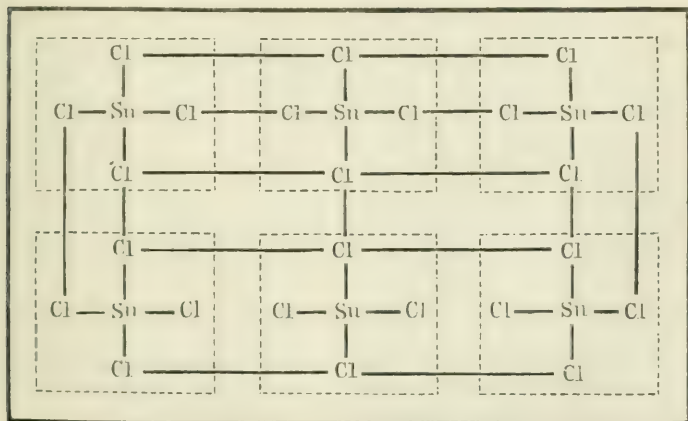


where x, y, z may or may not have the same value, and are probably of considerable magnitude. He considers that these groups are built up in virtue of the "Residual Affinity" which he holds to be characteristic of the negative elements. Such a group represented graphically would appear thus :—



This process of construction would be continued according to the value of x in $\boxed{\text{SnCl}_4}_x$.

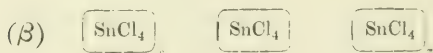
If a value of $x=6$ be assumed, the aggregation might be completely represented thus :—



Another group might be $(\text{SnCl}_4)_{10}$; another $(\text{SnCl}_4)_{12}$; &c. Then to call stannic chloride homogeneous, if thus composed of aggregates of varying complexity, is to use the term in an approximate and statistical sense, or subject to a reservation that it applies only to the ultimate molecules and not to the aggregates they form. The main purpose of this conception is the vivid realization of a condition of elephantine stability, one that shall afford a foundation for the dissociation processes which are associated with electrolytic conductivity. Thus, when Armstrong discusses the effect of water on the conductivity of the halogen acids, he submits the view that the dilution improves the conductivity by decomposing the more complex molecules; and generally he concludes, when the molecular conductivity is low, then there are big molecular aggregates. The liquid stannic chloride would consist of massive groups. This conception is fruitful, and explains many phenomena. But a simpler explanation may serve these purposes as effectively. It thus becomes of interest to consider whether it is necessary to adopt this view of the complex aggregates in the place of the simple molecular composition, whether stannic chloride is composed



or



In consideration of this question, it may be advanced that stannic chloride in the gaseous condition does consist in molecules represented as in (α) .

But it may be urged that some gases which have at high temperatures simple constitutions have at lower temperatures more complex ones. Thus nitrogen peroxide is " NO_2 " at high, and gradually passes into " N_2O_4 " at low temperatures. Mallet has observed that hydrofluoric acid is " H_2F_2 " just above its boiling-point. The density of acetic-acid vapour corresponds to a molecule $\text{C}_3\text{H}_6\text{O}_3$ within a few degrees of its boiling-point, and then, as the temperature rises, rapidly diminishes to a density which gives the molecular weight of 60.

Do, then, these observations lead by induction to the result that, as the vapour of $\boxed{\text{SnCl}_4}$ is condensed into a liquid, the molecules coming nearer and nearer coalesce into complex aggregates? If this induction be correct, then the liquid must have the constitution β .

But the induction is based upon a fallacy. It does not follow, in the cases cited, because the densities rapidly increase, relative to hydrogen, as the temperature falls, that therefore the molecules have also become greater. For these molecular weights are determined on the assumption that Avogadro's law is applicable to these substances in a vaporized and imperfectly gasified condition. Such an assumption is untenable; it is, as Prof. J. J. Thomson emphasizes in his lectures on the Properties of Matter, more rational to conceive that the vapours do not contain equal numbers of molecules. The statements that nitrogen peroxide is " N_2O_4 ," that hydrofluoric acid is " H_2F_2 ," that acetic acid is " $\text{C}_3\text{H}_6\text{O}_3$,"* are tainted with this fallacy; and the taint vitiates the induction that leads to the conception (β) as the constitution of liquid stannic chloride.

Moreover, positive evidence in favour of the simpler concept is supplied by the simplicity of the results obtained for the molecular weights of solids and liquids, as determined by the extent to which they lower the fusing-points and the vapour-pressure of solvents (Raoult).

On this ground the statement made as to the constitution of gaseous stannic chloride may be extended so as to include the liquid condition, provided of course a necessary degree of cohesion sufficient to account for the viscosity of the liquid be allowed between these simple material particles the molecules



And, again, it may be maintained that the condition (α) presents a prospect of greater stability than (β). For an inspection of the graphic representation of the group $[\text{SnCl}_4]$

shows that, whereas according to (α) the chemical homogeneity is preserved solely by the attractions of the respective atoms of tin for their four respective atoms of chlorine, according to (β) this attraction is opposed "by the straining of the chlorine atoms at the chlorine atoms of the adjoining molecules."

Thus, then, on account of the greater stability represented in the simpler view, on account of the evidence in its favour, on account of the absence of satisfactory arguments to prove the existence of the hypothetical complex aggregates, the simpler view (α) will here be taken and the stannic chloride will be considered as strictly homogeneous; *sic equaliter* for the other-mentioned nonconductors. And it is advanced that every substance thus strictly homogeneous is a nonelectrolyte on account of that very homogeneity. This homogeneity is a

* Horstmann, *Annalen*, clxviii. VI. sup. 53.

function of the chemical stability. Indeed the problem of electrolysis is at its foundation a chemical one; but at this, its foundation, the chemical problem resolves itself into an anterior physical one, namely the laws that govern the interaction, the attraction of atoms at atomic distances. "The scientific aim of the theory of electrolysis has been stated by F. Kohlrausch to consist in the reference of electrochemical phenomena to mechanical or electromechanical laws"* : herein must be the solution of the problem of chemical affinity.

To the question whether there is some physical property of pure water, pure hydrochloric acid, hydrofluoric acid, &c. which endows them with insulating-power, and the absence or difference of degree of which in fused salts admits of conductivity no successful answer has been given, though a great variety of attempts have been made. Doubtless viscosity is a factor in the result, and Faraday's law of liquido-conduction is a statement of that fact. But the influence of viscosity is secondary rather than primary : all the electrolytes must have a degree of limpidity, and as the limpidity decreases so will the resistance increase. As examples, Kohlrausch's experiments on Silver Iodide†, Arrhenius's investigations of the actions of Fluidity on the Conductivity of Electrolytes‡ ; though these would have been improved by the use, as sole solvent, of some oily polyhydric alcohol. But limpidity, as is seen in the various nonconducting pure liquids, does not involve electrolysability. The destruction of the physical homogeneity, and generally the change of physical properties which must occur when stannic chloride is heated from 16° C. to 112° C., its boiling-point, has not apparently any influence, and certainly not within the limits of delicacy of my experiments, on its nonconductivity.

To sum up : It has been advanced that the fact that stannic chloride is homogeneous, chemically homogeneous, accounts for its nonconductivity : similarly for the other nonelectrolytes. To continue : It will be demonstrated how the results obtained show that where this chemical homogeneity is destroyed, where the whole or part of the stannic chloride enters into combination so that molecular interchanges, akin to those which Williamson so vividly portrayed in his epoch-making papers on the Theory of Etherification, can occur, then the power of electrolytic conductivity is developed. The validity of this conclusion will be most cogently established by answer-

* Report on the Present State of our Knowledge in Electrolysis and in Electrochemistry. W. N. Shaw, M.A. (Brit. Assoc. 1889).

† Pogg. Ann. 1876, p. 159.

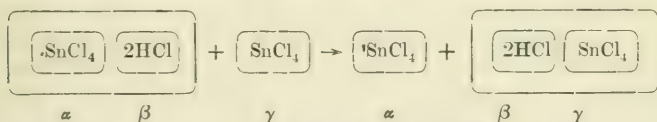
‡ *Kongl. Vetenskaps-Akad. Fordhandlingar*, 1885.

ing the following question: Whereas hydrochloric-acid gas, alcohol, ether, aqueous hydrochloric acid, sulphuretted hydrogen and alcohol, render stannic chloride an electrolysable liquid, why do not chlorine, sulphuretted hydrogen, chloroform, the various solids mentioned in Part I., exert a similar influence?

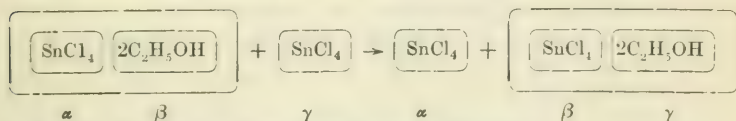
The answer is, that the former enter into chemical combination, the latter do not. To quote the concluding sentence of Part I., the latter class of substances "producing no effect on the chemical homogeneity of the stannic chloride, which remains merely stannic chloride, are without influence on its electrical conductivity:" a collection of unit particles, $\boxed{\text{SnCl}_4}$,

even where mechanically interspersed with foreign substances, do not conduct. But when hydrochloric-acid gas, alcohol, ether, hydrochloric-acid solution, sulphuretted hydrogen and alcohol, are added, electrolytic power is developed. Here, however, there is no longer chemical homogeneity.

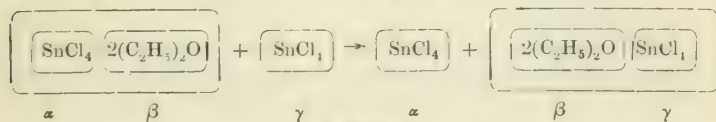
The stannic chloride charged with hydrochloric-acid gas must contain a collection of molecules of the double chloride $2\text{HCl} \cdot \text{SnCl}_4$ interspersed amongst molecules of stannic chloride. There is here manifestly the potentiality of a continual condition of interchange between the combined and uncombined stannic-chloride molecules; a condition of dynamical equilibrium maintained by changes of this nature:—



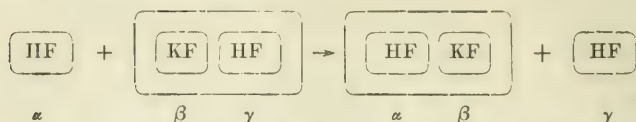
The similar phenomenon is repeated under the influence of absolute alcohol; here the alcoholate $\text{SnCl}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$ is formed and dissolved in the excess of alcohol. The equilibrium would depend on, here, the interchange of the combined alcohol molecules for the uncombined:—



Similarly for the etherate $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$:—



The idea of examining the influence of these liquids proceeded from a study of Moissan's* work on liquid hydrofluoric acid; it seemed that the conductivity he developed was due to such an interchange as:—



and it was conceived that if a similar condition of dynamical stability could be produced in stannic chloride, conductivity would be developed. The results have justified the induction. The delicate observations made by Kohlrausch on the resistance of pure water, and the effect of exposing it to the atmosphere of a room charged with tobacco-smoke, are explicable on the same lines; the water would absorb traces of carbonic acid and of the basic products, which in turn would form hydrates, and then there would result a similar condition of interchange.

The generalization may now be provisionally stated:—that such an antecedent condition of dynamical equilibrium is absolutely essential to the development of the power of electrolytic conductivity. With no great difficulty, it would be possible in terms of

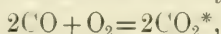
- (1) the number of such interchanges per unit of time,
 - (2) the degree to which the stability of the original unelectrolysable molecule is disturbed by each interchange,
- to establish a dynamical theory to explain the influence of (a) the concentration, (b) the temperature, on the conductivity of electrolytes; and for this purpose would be needed accurate measurements of the resistance of solutions (say, of the tetrachloride in alcohol, in ether, and of their temperature-coefficients). The results would emphasize the great value of some dynamical explanation of chemical action, and the influence of mass and temperature on its course.

The differences observed in the action of

- (1) dry sulphuretted hydrogen on stannic chloride,
- (2) dry sulphuretted hydrogen on stannic chloride in chloroform solution,
- (3) dry sulphuretted hydrogen and stannic chloride on water,
- (4) absolute alcohol on sulphuretted hydrogen and stannic chloride,
- (5) dry sulphuretted hydrogen on ether and stannic chloride,

* An account of Moissan's work is given in 'Nature,' vol. xxxvii. (1887-8); Moissan considers the potassium fluoride to be the electrolyte.

cannot fail to be suggestive. At present it may be noted that "where there exists an aptitude for directed decomposition," such as is involved in the above dynamical conception, and such as exists in the aqueous or alcoholic solution of stannic chloride, there sulphuretted hydrogen at once precipitates stannic sulphide; whereas between the dry sulphuretted hydrogen and stannic chloride there is found only a small quantity of addition compound ($\text{SnCl}_4 \cdot 5\text{H}_2\text{S}$), which, when agitated into a condition of instability by elevation of temperature, gives the stannic sulphide observed by Dumas. This influence of alcohol on stannic chloride and sulphuretted hydrogen is typical of that of catalytic agents in general; and the explanation here suggested is of wide application. The phenomena discovered by Prof. Dixon, to whom I am indebted for a complete list of the published papers on the action of dry substances, are of a parallel nature. He found that the combination of dry carbon monoxide and dry oxygen,



occurs only in the path of the spark, but that when the gases are moist the combination is explosive. Again, Dixon has shown that, in the combustion of carbonic oxide and hydrogen, the influence of the steam is not of a physical but of a chemical nature†. The inactivity of dry hydrochloric acid and dry oxygen, of dry hydrobromic acid and dry oxygen, and their activity in the presence of water is of the same nature‡ (Richardson). The observation, made by Pringsheim§, that dry chlorine and dry hydrogen do not combine in sunlight, but that the presence of a small quantity of water is sufficient to determine their combination, is quite parallel. Baker has proved that some dry solids are incombustible in dry oxygen, though he finds that others are combustible||.

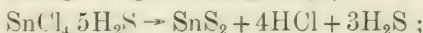
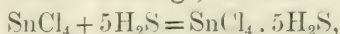
It cannot be maintained as a law of nature that no two pure substances, AB, DC, combine; either



possibly passing through the stage



As an example of such a change, we have



* Phil. Trans. 1884.

† Journ. Chem. Soc. 1886, p. 94.

‡ Journ. Chem. Soc. li. p. 803.

§ Wied. Ann. xxxii. p. 384.

|| Phil. Trans. 1888, "A."

but here, as in all the above cases, the catalytic agent, by producing a condition of dynamical equilibrium, greatly facilitates the change.

Further instances of the precise similarity between the action of catalytic agents and of those substances which are capable of endowing nonconducting liquids with the power of conduction will doubtless be found, and further proof analogous to those advanced here in the case of stannic chloride of the strict parallelism between the phenomena, of the birth of electrolytic power and of enhanced chemical activity, will trace these effects back to an identity of cause, the setting up of a condition of dynamical equilibrium.

Emmanuel College, Cambridge.

LVI. *The Theory of Osmotic Pressure and its bearing on the Nature of Solutions.* By SPENCER UMFREVILLE PICKERING, M.A.*

NO one can doubt the mathematical correctness of the conclusions which Arrhenius, van't Hoff, Ostwald, and others draw from the premisses with which they start in their arguments respecting osmotic pressure, nor can we doubt the value of connecting numerous actions with one and the same cause, or that there are a large number of instances in which the observed facts are in substantial agreement with their conclusions. But we may, I think, legitimately doubt whether the premisses of the arguments are sound, whether the conclusions harmonize as well as they should with experimental data, whether the theory is more than a mathematical exercise, or more than a convenient working hypothesis of a rough character, instead of being, as its supporters maintain, an hypothesis established so firmly that we may build upon it a physical theory of solution.

The direct measurement of osmotic pressure has been made in but a few cases, and those cases are ones in which the substances examined are eminently unfitted for showing the presence of any chemical action which may be present. Of the phenomena correlated with osmotic pressure, the lowering of the freezing-point of a solvent by the addition of foreign substances is the one which has received the greatest attention, thanks to Raoult's classical work, and is the one which forms the main support of the theory.

In examining the experimental facts the following questions must be asked, and if the theory is correct they must be answered in the affirmative.

* Communicated by the Physical Society: read March 7, 1890.

(1) Is the molecular depression—using this term to mean the lowering of the freezing-point produced by one foreign molecule on 100 *molecules* (not *parts by weight*) of the solvent—a constant, whatever the foreign substance is, provided that the amount of the latter is not greater than that which would give a pressure equal to that produced by it in the gaseous state at the same temperature?

(2) Are such deviations from regularity, as are observed in exceptional cases, in the direction in which they should be according to the theory?

(3) Is the depression a constant whatever the solvent is?

(4) Is the depression constant when the proportions of the solvent and dissolved substance are varied within the limits mentioned in (1)?

(5) When stronger solutions are taken, is the deviation from regularity in the direction in which it should be according to the theory?

(6) Is the deviation always in the same direction, and always regular?

I believe that I can show that the answer to every one of these questions is an unqualified No.

The main facts of the case as elucidated by Raoult's work are that, when various substances are dissolved in

Benzene,
Nitrobenzene,
Ethylene dibromide,
Formic acid,
or Acetic acid,

the molecular depression is about $0^{\circ}63$, though there are a few substances in each case which give an abnormal depression of about half this amount.

With water the molecular depression is generally $2^{\circ}06$, but in many cases approximates to $2^{\circ}61$, values which Raoult takes to be three and four times $0^{\circ}63$ ($1^{\circ}89$ and $2^{\circ}52$) respectively. Abnormally low values are in the same proportion to the normal ones as with other solvents; they are about $1^{\circ}03$ (half of $2^{\circ}06$), and are obtained with some inorganic substances, and with the majority of organic substances at present investigated.

All these determinations apply to solutions containing about 1 molecule to 100 molecules of the solvent, and are, therefore, three or four times stronger than they should be in order to be comparable with gases under ordinary conditions. We shall have to decide whether the discrepancies which they

show are such as could be reasonably attributed to increasing the pressure from one to three or four atmospheres.

Influence of the Nature of the Dissolved Substance.

The half values obtained in many cases are explained by the duplication of molecules, owing to the solutions not being sufficiently dilute; that is, an additional pressure of two or three atmospheres will cause the vapour-densities of hydrochloric acid *, methyl, ethyl, amyl, and butyl alcohols †, benzol, and many other substances to double themselves (assuming that they retain their gaseous condition). This may be so, but direct determinations cannot be, or have not been, made.

Leaving these abnormal values for the present, we find that the normal ones exhibit the following variations:—

Solvent.	Number of instances investigated.	Variation in the value of the depression ‡.
Acetic acid	57	30 per cent.
Formic acid	9	14 „
Benzene.....	41	12 „
Nitrobenzene	13	7 „
Ethylene dibromide.....	5	2 „
Water	59	60§ „
„ (with organic substances) ...	29	40 „

These variations appear somewhat too large to be attributed to the fact that we are working at two or three more atmospheres of pressure than we should be.

It is noticeable that the organic solvents, except acetic acid, give comparatively constant results, but that, as soon as we come to the inorganic solvent water (which we know shows a much greater tendency to form “molecular” compounds than the other liquids), we get a much larger variation, and the following values || will justify the assumption that when other solvents of a similar nature are examined, still greater variations will be observed.

* Solvent, Acetic acid (Raoult, *Ann. Chim. Phys.* [6] xi. p. 72, from which paper this and other values quoted here are taken).

† Solvents, Benzene, &c.

‡ Percentage on the lowest value.

§ Omitting borax, where the value is exceptionally high.

|| Chem. Soc. Trans. 1890. The values selected refer to solutions of the same strength as those used by Raoult. The results with calcium nitrate and chloride are as yet unpublished.

Solvent.	Dissolved substance.	Depression*.	Variation*.
			Per cent.
Tetrahydrate of sulphuric acid.	Water.	0.08	100
Do.	Sulphuric acid.	0.04	
Monohydrate of sulphuric acid.	Water.	0.02	100
Do.	Sulphuric acid.	0.01	
Sulphuric acid.	Water.	0.07	500
Do.	Sulphuric anhydride.	0.42	
Hexahydrate of calcium chloride.	Water.	0.003	233
Do.	Anhyd. calc. chlor.	0.010	
Tetrahydrate of calcium nitrate.	Water.	0.007	100
Do.	Anhyd. calc. nitrate.	0.015	

As an instance of a similar character we may quote Heycock and Neville's determinations of the depression of the freezing-point of sodium by various metals †.

Metal added.	Molec. depression.
Gold	4.5
Thallium	4.3
Mercury	4.5
Cadmium	3.0
Potassium	3.6
Lithium	1.3
Lead	4.6
Indium	3.5

The variation here is 260 per cent.

If such variations are not too great to be attributed to an excess of two or three atmospheres' pressure (and I certainly think they are), they are undoubtedly too great to permit of a theory being founded on the assumption that they are constant.

It may be noted also that Heycock and Neville's determinations with indium, gold, and thallium extended to solutions as dilute as the gases from these metals would be (if their molecules are diatomic), and that even with these "ideal" solutions the variation amounted to 60 per cent.; had lithium and cadmium been similarly investigated we should, no doubt, have found as great a variation as that quoted above with the stronger solutions.

* Most of these values are but approximations.

† Chem. Soc. Trans. 1889, p. 667. The values refer to solutions containing as near as possible one atom of the foreign metal to 100 Na.

Direction of the Deviations with Dissolved Substances which give Abnormal Values.

The abnormally low values (*i. e.* half values) which some dissolved substances give are attributed, as has been mentioned, to the polymerization of their acting molecules, and the abnormally high values which some solvents give are, in the same way, attributed to a polymerization of the solvent molecules. This view is accepted by both the supporters and the opponents of the osmotic pressure theory.

In the case of dissolved substances which give abnormally high values (*i. e.* double values), the supporters of the theory hold that these substances are dissociated into their ions, and in this view their opponents cannot agree with them.

The first point to settle, is whether there are any abnormally high values (given by dissolved substances), and it appears to me that there certainly are none.

In the case of the five organic solvents examined, the substances giving the higher and lower values are in the proportion of 100 to 16, and here there can be (and is) no question as to which are the normal ones; even if in the case of water these proportions were reversed, it would be inconsistent to term the lower values the normal ones; but the proportions are actually not reversed, the substances giving high values being to those which give the lower ones in the proportion of 100 to 76. I fail to see therefore what grounds there are for saying that there are any abnormally high (double) values at all, or what need there is for calling in such a theory as that of dissociation into ions*.

Indeed, there is a distinct difficulty, if not impossibility, in calling the lower values ($1^{\circ}03$) the normal ones; for the normal value with other liquids is $0^{\circ}63$, and the excess in the case of water could only be explained by the water molecules being more complex than those of other liquids in the pro-

* Van't Hoff's statement as to Raoult's position respecting the high and low values of substances in water is certainly remarkable; he says (Phil. Mag. 1888, xxvi. p. 99), "Raoult did not discover the existence of so-called normal [meaning small] molecular depression of freezing-point and lowering of vapour-pressure until he investigated organic compounds; their behaviour is almost without exception regular." As a matter of fact, Raoult investigated organic substances first (*Ann. Chim. Phys.* 1883 [5] xxviii. p. 133), and when he subsequently (*ibid.* 1884 [6] xi. p. 81) found that inorganic substances gave higher values, he did not hesitate to call these latter the normal ones.

If we reverse the application of the word normal, we shall have to admit that of the 150 substances examined in water, not one gave an abnormally low value. A most improbable admission.

portion of 1.03 to 0.63; in other words, that the water molecule is $1\frac{1}{2}$ H_2O , and that the atomic theory is wrong.

The theory of dissociation into ions is, for many reasons, unacceptable to most chemists, and its application to the results at present under discussion affords, I think, some of the strongest arguments against its acceptance.

If the higher values in the case of water are due to dissociation, we must conclude that all the stronger acids (*e.g.* hydrochloric, sulphuric, and nitric acids) are nearly entirely dissociated, whereas the weaker ones (*e.g.* hydrocyanic, sulphurous, and boric acids) are not so; and similar conclusions must be drawn respecting the alkalis and salts. In fact, we shall be driven to conclude that the more stable the compound is the more easily is it dissociated, and that too by an agent, water, which has, *ex hypothesi*, no action beyond the diluting effect of its mass. Is it possible to maintain that sulphurous acid *exists* intact in solution, while sulphuric acid, which is formed from it and molecular oxygen, with the evolution of 55,000 cal.*, and which must, therefore, be by so much the stabler body of the two, is entirely dissociated? Is it possible to maintain that hydrochloric acid is entirely dissociated at a pressure of three or four atmospheres when we know as a fact that it can exist undissociated at a pressure of only one atmosphere †?

Indeed, it appears to me that if we acknowledge such a dissociation we must deny the principle of the conservation of energy. Thus, to take one instance out of many, the molecules of hydrogen and chlorine must ‡ be formed from their constituent atoms with a considerable development of heat, say $+x$ and $+y$ cal. respectively, and they react with each other to form 2HCl with a further development of 44,000 cal.; if this 2HCl , when dissolved in water, be entirely dissociated into its atoms, it must *absorb* 44,000 $+x+y$ cal., whereas, as a matter of fact, it *evolves* 34,630 cal.: hence there has been a creation of $(78,630 + x + y)$ cal. out of nothing,

* If atomic oxygen were taken, as it should be, the heat evolved would be much greater.

† In acetic acid hydrochloric acid is, according even to the supporters of the theory, not only not dissociated into its ions, but even not dissociated into its fundamental molecules, it being present as 2HCl .

‡ I think that we may say "must." If they were formed with absorption of heat it would mean that the atoms repel each other, and such atoms would, therefore, never combine. When we call a molecule endothermic, we merely mean that it is formed from its constituent atoms with a smaller development of heat than some other compound of the same atoms, not that it is formed from these atoms with an *absorption* of heat.

and that, too, through the agency of the water, which is assumed to have no action at all.

Influence of the Nature of the Solvent.

It is found that the nature of the solvent, instead of being without influence on the results, as it should be according to the osmotic-pressure theory, is one of the main factors in determining them.

Thus, for instance, sulphuric and hydrochloric acids give the normal high values when dissolved in water, but solutions of the *same* strength in acetic acid show the abnormal half-values: formic and benzoic acids, methyl, ethyl, butyl, and amyl alcohols, as well as phenol, all give normal depressions with acetic acid, but abnormal ones with benzene. Many other instances of a similar character may be selected from Raoult's data, but none of them show the influence of the nature of the solvent in such a forcible manner as the following:—

	Molec. Depress.
H ₂ O dissolved in 100 H ₂ SO ₄	1·072
„ „ 100 (H ₂ SO ₄ H ₂ O)	0·02
„ „ 100 (H ₂ SO ₄ 4H ₂ O)	0·08
„ „ 100 (CaCl ₂ 6H ₂ O)	0·003
„ „ 100 (Ca(NO ₃) ₂ 4H ₂ O)	0·007
„ „ 100 (CH ₃ COOH)	0·55

The variation of this constant (?) calculated on the smallest value amounts to 35,600 per cent. Again,

H ₂ SO ₄ dissolved in 100 H ₂ O	2·15
„ „ 100 (H ₂ SO ₄ H ₂ O)	0·01
„ „ 100 (H ₂ SO ₄ 4H ₂ O)	0·04
„ „ 100 (CH ₃ COOH)	0·31

Extreme variation 21,400 per cent. Similarly,

CaCl ₂ dissolved in 100 H ₂ O	2·773
„ „ 100 (CaCl ₂ 6H ₂ O)	0·010

Variation 27,600 per cent.; and

Ca(NO ₃) ₂ dissolved in 100 H ₂ O	2·50
„ „ 100 Ca(NO ₃) ₂ 4H ₂ O	0·015

Variation 16,600 per cent.

Such numbers can certainly not be accepted as constants, and the values are certainly largely dependent on the nature of the solvent*.

In the present instance the variation cannot always be taken as a proof of the incorrectness of the osmotic-pressure theory, for it may be perfectly legitimate to attribute it sometimes to the various complexity of the molecules of the solvent. But we cannot, however, do so in all cases, as for instance that of formic &c. acids in benzene and acetic acid, where the two solvents have been proved to act normally with the majority of dissolved substances. Yet, in any case, the absence of constancy means the absence of what would have been a strong argument in favour of the theory, and this absence must be felt all the more because there appears to be no simple numerical relationship between the very different values given above.

Influence of Proportions taken with very Weak Solutions.

My own recently published results (Chem. Soc. Trans. 1890, p. 331) with sulphuric-acid solutions form, I believe, the only series of determinations as yet made which would, from their number and precision, be at all likely to settle whether the molecular depression is really constant or not with very weak solutions; and the results here can leave little doubt but that it is not so.

Between 0 and 9 per cent. solutions the results are represented by what would with rough determinations appear to be a single line of typical straightness. The deviations from straightness in regions below 4 per cent. (about 0.8 H_2SO_4 to 100 H_2O) are less than $0^{\circ}\cdot 02$, and would, therefore, not have been revealed by determinations such as have been made by other investigators. From 4 per cent. to 0 the determinations (each being the mean of several observations) which I made show mean error of $0^{\circ}\cdot 0008$ at most, and the number of points determined is about 80; and the results obtained leave no doubt but that the apparently straight line is really composed of four distinct lines, three of which are straight, meeting at (generally) well marked angles at the percentages of 1.0, 0.35, and 0.07 respectively.

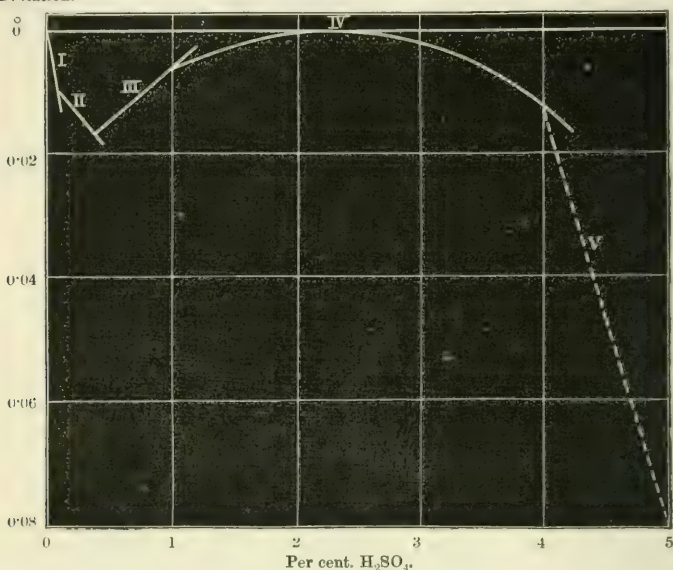
The relative magnitude of these changes is best illustrated by drawing a straight line from the freezing-point of water

* Combining the variations due to different solvents with those due to different dissolved substances, we get a variation of 153,000 per cent. ($4^{\circ}\cdot 6$ to $0^{\circ}\cdot 003$).

to that of a 2·5 per cent. solution (H_2SO_4 to 200 H_2O ; this was selected merely because at this percentage the diagram attains the highest relative point) and plotting out the deviations of the observed freezing-points from this line. The accompanying figure illustrates the result. The deviation

Deviation of the Freezing-points of weak solutions of Sulphuric Acid from regularity.

Deviation.



from straightness amounts to at least 20 times the mean experimental error, and 28 per cent. of the total depression. Even if we draw our straight line from a solution of 0.44 ($\cdot 08 \text{ H}_2\text{SO}_4$ to 100 H_2O) per cent. strength—in which the sulphuric acid would be as much expanded as it would when a gas at ordinary pressures—the aberration, at 0.7 per cent., amounts to 0.008, or 20 per cent. of the total depression.

The molecular depression calculated from these results, together with others obtained with stronger solutions, are given in the following table:—

Depression of the Freezing-point of Water produced by the addition of Sulphuric Acid.

Per cent. H_2SO_4 .	Mols. H_2SO_4 to 100 H_2O .	F.-P.	Molecular depression.
0.068	0.0125	— 0.0369 ^o	2.95*
0.3618	0.0667	— 0.1580	2.37
0.44	0.0811	— 0.1874	2.31
1.057	0.1961	— 0.4214	2.15
2.500	0.4708	— 0.9825	2.09
4.021	0.7692	— 1.600	2.08
6.000	1.1855	— 2.520	2.15
8.585	1.724	— 3.456	2.00
18.492	4.167	— 11.83	2.84
29.526	7.692	— 34.00	3.74
37.701	11.111	— 72.63	6.54

The depression with solutions weaker than H_2SO_4 to 100 H_2O varies between $2^{\circ}08$ and $2^{\circ}95$, 42 per cent., and even between 0.44 and 0 per cent. it varies from $2^{\circ}31$ to $2^{\circ}95$, a variation of 28 per cent., numbers which can give no grounds whatever for the statement that the depression, even with these very weak solutions, is independent of the strength.

The only other determinations which, so far as I know, exist with solutions containing less than one dissolved molecule to 100 of the solvent, are those of Heycock and Neville (*loc. sup. cit.*) with certain alloys. Selections from those series which were most fully investigated supply the following data:—

Solvent.	Dissolved substance.	Molecular depression.
100 Na	0.114 Au	5.45 ^o
"	0.296 "	4.74
"	0.966 "	4.54
"	0.097 Cd	3.92
"	0.391 "	3.71
"	0.648 "	3.17†

* With still weaker solutions the molecular depression is somewhat greater: with a 0.005 per cent. solution (0.0009 H_2SO_4 to 100 H_2O) the value found was $3^{\circ}4$, but the total depression here is so small that I have not included it or similar values in the table.

† With thallium, mercury, sodium, and indium, the depression was more constant, but the data were less complete.

Direction of the Deviations from Constancy with Stronger Solutions.

According to the theory of osmotic pressure the proportionality between pressure (lowering of freezing-point) and amount of substance dissolved will hold good, as has been remarked, only for very weak solutions. With stronger solutions the dissolved molecules will be brought within the sphere of each other's attraction and will, therefore, exert an abnormally small pressure; that is, they will lower the freezing-point of the solvent to an abnormally small extent*.

But in every case at present known exactly the reverse is the case. Stronger solutions exhibit an abnormally *large* depression, and the freezing-points fall at an increasing instead of a diminishing rate. The table given above illustrates to what extent this takes place in the case of solutions of sulphuric acid in water, the molecular depression increasing from 2°·08 to 6°·54 (213 per cent.), and the examination of six other curves from the sulphuric-acid series, and two of a series with calcium nitrate, supplies us with eight other instances of a similar character. The results may be summarized thus:—

Solvent.	Dissolved substance.	Molec. depression.	Increase.
100 H ₂ SO ₄	1 to 33 H ₂ O	1°·072 to 1°·253	17 percent.
100 H ₂ SO ₄	1 to 5·8 SO ₃	0°·422 to 0°·634	50 "
100 (H ₂ SO ₄ H ₂ O)	1 to 50 H ₂ O	0°·02 to 0°·31	1,450 "
100 (H ₂ SO ₄ H ₂ O)	1 to 50 H ₂ SO ₄	0°·01 to 0°·197	1,870 "
100 (H ₂ SO ₄ 4H ₂ O)	1 to 400 H ₂ O†	0°·078 to 0°·108	39 "
100 (H ₂ SO ₄ 4H ₂ O)	5 to 60 H ₂ SO ₄ †	0°·27 to 0°·42	55 "
100(Ca(NO ₃) ₂ 4H ₂ O)	1 to 150 H ₂ O	0°·007 to 0°·326	45,600 "
100(Ca(NO ₃) ₂ 4H ₂ O)	1 to 33Ca(NO ₃) ₂	0°·015 to 0°·179	11,000 "

It is true that these results have only recently been placed at the disposal of the supporters of the osmotic-pressure theory, but it is otherwise with the following values in the case of alcohol (Raoult, *Compt. Rend.* xc. p. 863) and calcium chloride (Hammerl, *Wien. Sitzungsber.* lxxviii. p. 59) §:—

* The same will hold good if we attribute dissolution to the balancing of the physical attractions of (1) solvent for solvent molecules, (2) dissolved for dissolved molecules, and (3) solvent for dissolved molecules. The stronger the solution the greater will be (2), and, consequently, the less will (1) be counterbalanced.

† With 60 H₂O the depression is 0°·067, so that it first decreases and then increases.

‡ With 1 mol. H₂SO₄ it is 0°·40.

§ In each case I give the values as determined from my own results, but these are in good accord with those referred to above.

Solvent.	Dissolved substance.	Molec. depression.	Increase.
100 H ₂ O	1 to 7 CaCl ₂	2.773 to 6.9	150 per cent.
100 (CaCl ₂ ·6H ₂ O)	1 to 800 H ₂ O	0.003 to 0.099	3200 "
100 H ₂ O	1 to 13 C ₂ H ₅ O	1.11 to 1.18	6 "

The increase in the case of alcohol is small, but still there is an increase, and not a decrease ; while in the case of water in the hydrate of calcium chloride the increase is almost the greatest at present known.

Irregularity of the Deviations with Weak Solutions.

That the deviations from constancy are not regular, and are not even always in the same direction, will be seen on referring to the results with sulphuric acid dissolved in water (p. 499) ; the depression in the freezing-point of the tetrahydrate, both by water and sulphuric acid, supplying two other instances of a similar character.

Since every fact which can be used to test whether the theory of osmotic pressure is a true explanation of the nature and behaviour of solutions, either fails to give any evidence in its favour, or else gives evidence directly opposed to it—evidence, often, of the strongest possible character—this theory can certainly not yet be regarded as established.

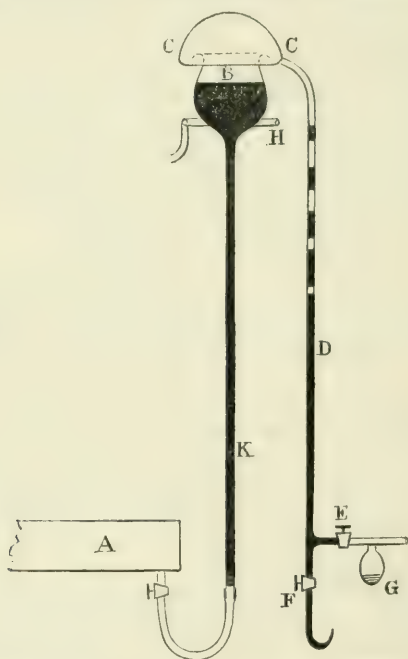
LVII. *A Mercury-still for the Rapid Distillation of Mercury in a Vacuum.* By FREDERICK J. SMITH, M.A., Millard Lecturer in Mechanics and Physics, Trinity College, Oxford*.

WHEN mercury is distilled in a vacuum, in the usual apparatus, a large portion of it when vaporized, on reaching the internal domed surface of the bulb in which the operation is conducted, forms itself into minute spheres, which grow heavy and run down the inside of the bulb ; and only a small quantity of the metal finds its way into the central tube, from which it is caught for use.

The advantage of the new form of vacuum mercury-still, of which I venture to give an account, is that all the mercury, which condenses in the head of the bulb, is prevented by its shape from returning to the mercury from which it has been separated by heat. This is not the case in the mercury-still of Weinhold, or Clark, or in those stills in which only the mercury which collects in the eduction-tube is caught, as in

* Communicated by the Author.

the beautiful new form of apparatus, devised by Messrs. Dunstan and Dymond, for the purification of small quantities of mercury (*suprà*, p. 367). In the former of these instruments, some portion of the mercury-vapour condenses on the surface of the bulb and then falls back to the mass of mercury from which it has just been separated. The mercury-still which is described in the following lines has been constructed with a view to obtain a more rapid yield of pure mercury than stills of this class have hitherto been capable of producing. The yield of mercury from the new form of still is about four times as great as that from one of the old pattern, the consumption of gas in each case being the same. The construction and method of using the still are as follows:—B K is a bulb and tube about 34 inches long, supported on a stand not shown; the bulb has a ring-shaped channel, C C, round its upper end; into this channel a piece of “Sprengel” tube, D, is fused. This is furnished with two



taps of glass, E and F; E is in connexion with a water-jet pump, F is terminated with a piece of bent tube. A is a cistern for holding the mercury which is to be distilled. H is a ring of gas-jets.

The method of using the still is as follows:—The tap E is opened, F is closed; a water-pump then exhausts the whole system, and the mercury to be acted on rises from the cistern A. The cistern being large and shallow, only a slight change takes place in the height of the mercury in the bulb, when the level of the mercury in the cistern changes. While the pump is exhausting the ring of gas-jets is lit, and in about ten minutes, in the case of the still in our laboratory, the mercury fills the tube D, any metal which comes over being caught in the bulb G. The tap E is then closed and F opened; the still then continues to work by virtue of the vacuum formed by its own mercury. It has been found necessary to place a gas-regulator on the pipe which supplies the jets, as the change of pressure in the gas-mains is considerable. An automatic arrangement, depending for its action upon the height of the mercury in the cistern, shuts off the gas when the surface of the mercury falls below a certain point. In using stills of this class the mercury before distillation should be carefully freed from moisture, as a minute quantity of water will often cause a fracture in the heated tube or bulb.

LVIII. *On the Distribution of Flow in a Strained Elastic Solid.*
By CHARLES A. CARUS-WILSON, B.A., A.M.I.C.E.,
Demonstrator in the Mechanical Laboratory at the Royal Indian
Engineering College, Coopers Hill*.

IF a metal bar of uniform section throughout its length be subjected to uniform longitudinal stress, the elements of the bar will become distorted; if the strain should exceed the limit of elasticity the distortion will be partly permanent.

In consequence of the straining of the elements, every element will experience a displacement relative to three fixed axes in the bar; say ox parallel to the length of the bar, oy parallel to one side, and oz parallel to a second side, both oz and oy being at right angles to ox : such displacement is generally spoken of as “flow.”

It is clear that if the metal be homogeneous, the stress uniform, and the section at right angles to the axis everywhere the same, an element will experience a displacement at right angles to the planes xoz , yoz proportional to its distance from these planes; since such displacement depends on the straining of the elements between it and these planes. Hence a bar with its sides originally parallel to ox will remain so

* Communicated by the Physical Society: read May 2, 1890.

after a certain amount of flow has taken place, and lines drawn on the sides respectively at right angles to and parallel to ox will remain so, since the displacement parallel to ox will be proportional to the distance from the plane yoz .

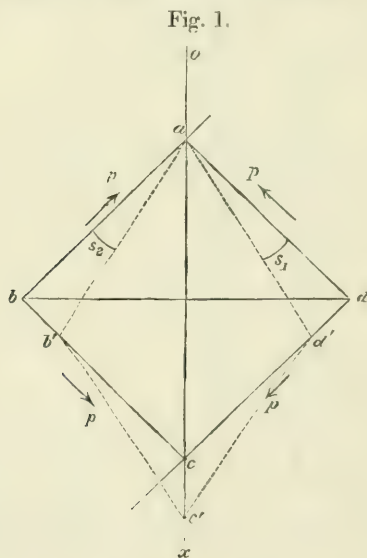
The question I propose to discuss is how to determine the distribution of flow when the section at right angles to ox varies in any way as we pass along ox .

I will for simplicity consider a plate in which the thickness parallel to oy is considerable compared with the thickness parallel to oz , and I will consider the displacements in the plane xoy .

We may take a plate in which there is a gradual reduction of section, in which there is what is commonly called a "shoulder," as in fig. 2.

It is required to determine the displacements in the plane of the paper—the plane xoy : in other words, supposing the plate covered with a series of lines parallel to ox and to oy respectively, it is required to determine the curvature of these lines due to flow.

The distortion of the elements is caused by the shearing-strain induced in the bar when subjected to longitudinal stress. Since this shearing-strain is a maximum at 45° to the axis ox of the bar, it will be convenient to consider the bar divided



into a number of small elements with sides making angles of 45° to the axis ox . Every such element as $abcd$ (fig. 1) will

be subject to a shearing-strain of amount $\frac{p}{n}$; *i. e.* the angle $b a d$ will be diminished by an amount $\frac{p}{n}$, where p is the intensity of the shearing-strain on the element, and n is the coefficient of rigidity of the metal. The effect of this shearing-strain on the element may be described as a rotation of $a d$ through an angle s_1 , and of $a b$ through an angle s_2 , where $s_1 + s_2 = \frac{p}{n}$; s_1 and s_2 may be equal, when the displacement of c will be wholly parallel to $o x$; or they may be unequal, when c will have a displacement parallel to $o x$ and a resolved displacement parallel to $o y$, which will be +ve or -ve according as s_1 is less than or greater than s_2 , and which will be a maximum if either s_1 or $s_2 = 0$.

The value of $s_1 + s_2$, and the ratio of s_1 to s_2 for any element, appears to be determined by the following considerations. If a side $a b$ of the element be produced in both directions so as to cut the sides of the bar, there is seen to be a tendency of that part of the bar below this line to slide over that part which is above. Assuming the resulting shearing-strain to be uniform over the length l_1 of this oblique section, the shearing-strain at any element in this direction, *i. e.* s_1 , will clearly be inversely proportional to l_1 ; s_2 will also be inversely proportional to l_2 , where l_2 is the length of an oblique section parallel to $a d$, and $s_1 + s_2$ will be proportional to $\frac{l_1 + l_2}{l_1 l_2}$ —say to $\frac{1}{\rho}$.

Suppose, now, we take a series of elements, $a_1 b_1 c_1 d_1$ — $a_2 b_2 c_2 d_2$ touching one another and lying across the bar. If we imagine the points a_1, a_2, a_3 , &c. fixed on a line parallel to $o y$, it is clear that the displacements of c_1, c_2, c_3 , &c. will be proportional to the sum of the shearing-strains in each element. If $s_1 + s_2$ is the same for each element, and $s_1 = s_2$, the points c_1, c_2, c_3 , &c. will remain on a line parallel to $o y$. If, however, $s_1 + s_2$ becomes greater as we approach the middle, and less again towards the further side, the points c_1, c_2, c_3 , &c. will be found on a line concave upwards; if $s_1 + s_2$ diminishes towards the centre these points will lie on a line concave downwards. If the strains should exceed the limit of elasticity the line through c_1, c_2, c_3 , &c. will be permanently curved.

If the points a_1, a_2, a_3, \dots , instead of being in one straight line have unequal downward displacements, the form of the curves obtained as above may be modified.

If, now, we consider a series of consecutive elements, $a_1 b_1 c_1 d_1$ — $a_1 b_2 c_2 d_2$, lying in a line parallel to $o x$, if $s_1 = s_2$ for

each element the points c_1, c_2, c_3 , &c. will continue to lie on a line parallel to ox , since the displacement of each of these points, due to the distortion of the corresponding element, is parallel to ox . But if as we descend from the first element we find s_1 becoming greater than s_2 , the points c_2, c_3 , &c. will have a displacement to the left which increases as we descend, so the line passing through c_1, c_2, c_3 , &c. will be bent; and if the shearing-strains become equal again on the lowest element, this line will be concave to the right.

Fig. 2.

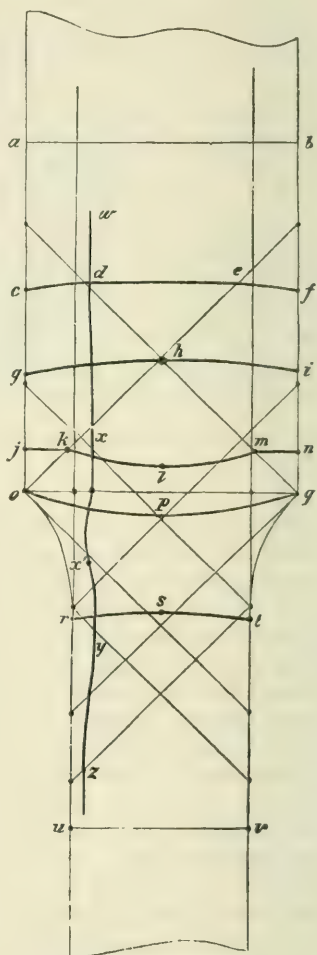
It thus appears that any horizontal line will be curved concave downwards if the sum of $s_1 + s_2$ is greater at the end of the line than in the centre, and *vice versa*, but that the line will remain straight if $s_1 + s_2$ is constant along its length, and $s_1 = s_2$.

Also that a vertical line will remain so if s_1 is everywhere equal to s_2 ; but if s_1 is $> s_2$, the line will be curved and concave towards the right, and *vice versa*.

We can now proceed to determine the curvature of the lines in the case before us.

Commencing at the upper extremity of the bar, fig. 2, a line such as ab will remain straight, because ρ is everywhere constant, and $l_1 = l_2$. The line $cdef$ will be curved concave downwards, since from c to d and from e to f ρ is less than it is from d to e (where it is constant and $l_1 = l_2$); de will therefore remain straight, and cd and ef curved as shown. The line gh will be concave downwards and curved along its entire length, since ρ gets less as we move away from h on both sides.

The line $jklmn$ will remain straight from j to k , since ρ is there constant and $l_1 = l_2$; from k to l ρ becomes



less and greater again from l to m , $k l m$ is therefore concave upwards; this line is straight from m to n , since ρ is constant and $l_1 = l_2$.

The line $o p q$ is curved concave upwards throughout the entire length, since ρ diminishes from o to p and increases from p to q .

The line $r s t$ will be concave downwards, since ρ diminishes from r to s and increases from s to t .

The line $u v$ will remain straight, since ρ is constant and $l_1 = l_2$.

To turn now to the curvature of the vertical lines. If we consider one of these as $w x y z$, from w to d $l_1 = l_2$, at x l_2 is $< l_1$, while at x' $l_1 = l_2$ again, so that from d to x' this line will be curved in convex towards $o x$. Again, at y l_2 is $< l_1$, and at z $l_1 = l_2$, therefore $x' y z$ is also curved in convex towards $o x$.

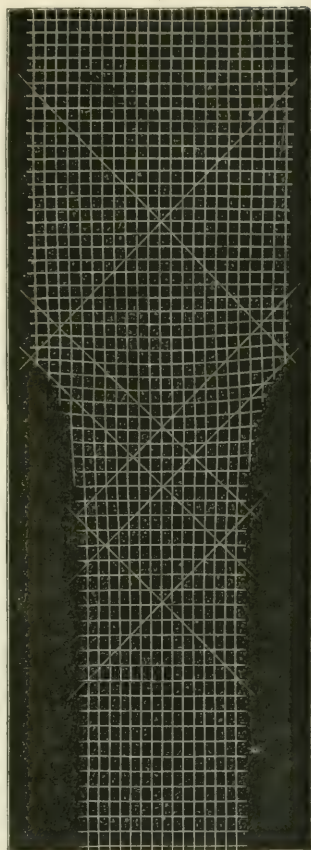
It would appear then that the horizontal lines will have three distinct changes of curvature, while the vertical lines will be pinched in above and below the shoulder.

To test the accuracy of these conclusions, I prepared a copper bar as shown in the following way. The sides and faces were very carefully planed and polished, and on one face I inscribed a series of vertical and horizontal lines in a lathe. I then strained the bar so as to produce a considerable permanent set. An impression was then taken from the bar, which is reproduced in fig. 3*.

By placing the eye very nearly in the plane of the paper and looking along the lines, the curvatures can be seen to follow very closely those sketched on fig. 2. I would specially draw attention to the partial curvature of such lines as $c d e f$ and $j k l m n$.

* The diagonal lines in fig. 3 were ruled on the impression to serve as lines of reference.

Fig. 3.



LIX. *On Sensitive Galvanometers.* By R. THRELFALL, M.A.,
Professor of Physics, University of Sydney, N.S.W.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

THOUGH I expect the matter will have been almost forgotten when this reaches England, I still desire, if possible, to meet some of the criticisms which have been levelled at me by Professor Gray in the *Philosophical Magazine* for February 1890, and by Professor Ayrton at the Physical Society on January 17th. Of Professor Ayrton's criticisms I have only as yet seen a report in 'Nature' for January 30, but since they appear in the main to coincide with Professor Gray's as nearly as I can judge, I will endeavour to reply to both at once.

In the first place, then, I must of course plead guilty to having made a mistake in arithmetic (to my shame be it said), and must express my thanks to Professors Ayrton and Gray for pointing it out. It now appears that instead of my success with the Gray galvanometer being a thousand times less than Professor Gray's, it is only about a hundred times less as compared with the performance in 1884, and three times less as compared with his results in 1889. As the matter is one which purely depends on instrument-making and experimenting, I can only say that I am very glad to find myself approach so nearly to Professor Gray. With respect to the much graver and more important charge that I have overestimated the performance of another type of galvanometer, I can only say that the mistake rests entirely with my critics, though very likely through my own fault in endeavouring to achieve conciseness of statement. That the galvanometer described did actually attain the sensitiveness quoted, viz. 5 divisions to 10^{-11} ampere of current, a fresh reference to my notebook amply proves. Neither in my paper on "The Measurement of High Specific Resistances," nor in the following one on the Specific Resistance of an Impure sample of Sulphur, have I given any data from which this value was computed. How, then, can Professors Ayrton and Gray have concluded that I was in error? Professor Ayrton, as I imagine, and certainly Professor Gray, have obtained their data from the resistance-measurements quoted; but it is purely gratuitous on their part to assume that these were the data used by me, and as a matter of fact they were not. In writing the paper, which pretended to be an account of an absolute measurement, I gave the maximum sensitiveness reached by the galvanometer in order to show that I had a good margin in the actual experiments, and was

not using the galvanometer at its limit of sensitiveness. Surely it is not necessary to remind such well-known experimentalists as my critics that an absolute measurement depending on the indications of an instrument at its extreme sensitiveness are always liable to objection. I find in fact from my notebook that the sensitiveness mentioned having been obtained, it was reduced (by lowering the control magnets) to meet the requirements of the work in hand. The resistance of the sulphur turned out to be much less than I had anticipated, for I had got three hundred and sixty small storage-batteries ready for the work, as well as some forty Clark-cells; so I reduced the number of cells and the sensitiveness of the galvanometer in what appeared to me at the time as the most advantageous manner. On reading the paper, however, I see that I was not so explicit (for the sake of brevity) as I might have been. I welcome a discussion on sensitive galvanometers, however, though it has been raised somewhat at my own expense, because I believe that the galvanometer-method has several advantages over the electrometer-method in high-resistance measurements. To this, however, I will not now refer, but will instead make some further remarks anent sensitive galvanometers.

My friend Mr. Boys, at the Physical Society some time ago, said that my quartz fibres were too long and thick. Well, that is a matter of opinion. I used the finest fibres that I could manipulate; and as I saw that I could handle a yard of them almost as well as an inch, I did not see why I should not reap the advantage of length. I saw Mr. Boys's fibres, and I do not think that he mounts much finer ones than I do, though as it is purely a matter of manipulatory skill I daresay Mr. Boys *can* mount finer fibres than I can. If I can persuade Mr. Gray to use quartz instead of silk as a means of suspension, I am sure he will live to bless me. While I am on this subject I will add, that if Professor Gray will reread my paper he will find he has been unjust to me in stating that I must have used the galvanometer near the limit of sensitiveness as the zero was "always on the move." He will find that the whole sentence runs thus:—"It is practically impossible to get a galvanometer of this degree of sensitiveness to work with a silk fibre, the zero being always on the move." Since I gave this as one reason for having adopted quartz, Professor Gray will, I think, see that his argument, in so far as it depends on the galvanometer being at its limit of sensitiveness, is baseless, and that his stricture is unmerited.

With respect to quartz fibres, I may say that I am forwarding a paper on this subject to you; but meanwhile I desire to

state here that I have gone back to Mr. Boys's method of preparing the quartz, which (as might have been expected) is much better than mine. I wonder how many people have any real idea of what a sensitiveness of "five divisions to 10^{-11} ampere" really means. From the glibness with which we talk of sensitiveness, I fancy the conception has not generally been really grasped. Let me give an illustration. We all look on the eye as perhaps our most sensitive organ. In the *Philosophical Magazine* for January 1889 is a paper by Professor Langley, in which an estimate is made of the minimum rate of expenditure of energy (by radiation) which can affect the eye. The estimates are of course rough and not very concordant, and there is some obscurity arising from the hoary-headed difficulty of distinguishing between work and rate of working. However, it follows from the data given, that an expenditure of work at the rate of 2.6×10^{-6} C.G.S. per second will affect the eye so as to produce vision when the light has a wavelength nearly that of the line A; while an expenditure at the rate of 2.6×10^{-11} (or 5.7×10^{-12} from another part of the paper) will produce the same effect if the light is green. Now the galvanometer I described had a resistance of nearly 16,000 ohms; and since 10^{-11} ampere produced a deflexion of five divisions, we may say that we could detect a current of 10^{-12} ampere (giving a deflexion of half a division). In this case a simple calculation (without arithmetical error) shows that the galvanometer absorbed work at a rate of about 1.6×10^{-9} ergs per second. Consequently the sensitiveness of the galvanometer may be said to stand half way between that of the eye for crimson and green light respectively.

I never intended to institute a comparison between Prof. Gray's form of galvanometer and the Thomson form: what I wanted was to get a workable instrument as easily as possible, and I found the Thomson form most easily manageable. Though the Gray form may be workable at the hands of such exceptionally skilful manipulators as its inventors, I do not think that for the ordinary run of experimentalists it is to be compared with the older form, and I certainly do not pin any faith to silk fibres a few inches long. Though, as Professor Gray remarks, his form of galvanometer possesses "solid advantages," as it certainly does, still it possesses also solid disadvantages, and these will, I think, in the long run be found to predominate.

I am, Gentlemen,

Yours obediently,

University of Sydney, N.S.W.,
March 7, 1890.

RICHARD THRELFALL.

LX. *Considerations on Permanent Magnetism.*

By M. F. OSMOND*.

IRON possesses at least two molecular states, α and β . α is soft iron, that is iron which has been annealed and cooled slowly. It changes into β during heating, at a certain critical temperature, and in part preserves this state during cooling, the more so the quicker the cooling and the larger the proportion of carbon, manganese, and tungsten that it contains. Some β iron is also produced during cold hammering. Iron deposited electrically is also of the β variety.

A bar of steel, allowance being made for the carburets and other compounds simply in mixture, can then be looked upon as an intimate mixture of α iron and β iron in relative proportions, which can change from point to point but are determinate at any point. That being so, let us consider β as forming in a steel bar a porous framework, not changing under the influence of currents and of magnets. On the other hand, let us look upon α as composed of particles polarizable under such influences. (The actual mobility of such particles, admitted by Hughes, appears from the sounds and changes of volume which take place during magnetization.) The particles α so polarized will form so many small elementary magnets, which the magnetizing force has displaced from their former normal position of equilibrium, and which tend to take up this position again so soon as the external force ceases to act.

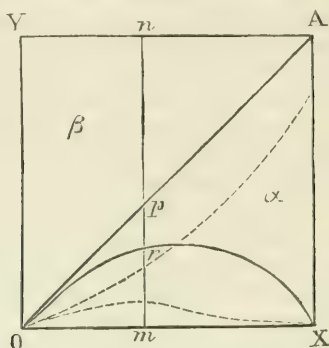
But in presence of the rigid network of iron β these polarized particles α are conceived as catching in the pores of the β structure, and immovable in this position, thus resulting in a permanent magnet. The temporary magnetism and the permanent magnetism determined by the action of a certain magnetizing force at a point of a bar will be therefore a function of the relation $\frac{\alpha}{\beta}$ at this point.

As an attempt to represent these ideas graphically, let there be a square, O A X Y, of which the side represents 100 parts. Every line $m n$ parallel to the axis of Y meeting in p the diagonal O A represents a steel containing $\frac{mp}{100}$ of iron α , $\frac{np}{100}$ of iron β .

At saturation the temporary magnetism, or rather the sum

* Communicated by the Physical Society: read April 18, 1890.

of the polarized particles, will be exactly equal to the whole of the iron α , *i. e.* to mp . α varying from 0 to $\frac{100}{100}$, the temporary magnetism will be represented by the diagonal O A.



As to the permanent magnetism, in regarding it as the relative number of particles of α which remain polarized after the cessation of the magnetizing force, it will be a fraction of mp , all the greater as $\frac{\alpha}{\beta}$ is smaller for the steel under consideration. In other words, the polarized particles α will be more immovable the closer the network β .

Under the supposition that the quantity mr of the particles α which remain polarized after the interruption of the magnetizing force (that is to say, the permanent magnetism as defined) is proportional to the percentage of iron β , $\frac{np}{100}$, we can write

$$mr = mp \times K \frac{np}{100},$$

K being a numerical coefficient equal to or less than unity.

Since

$$\begin{aligned} mp &= mO = x, \\ np &= 100 - mp = 100 - mO, \\ &= 100 - x, \\ y &= x \times K \frac{100 - x}{100}, \\ &= K \left\{ x - \frac{x^2}{100} \right\}. \end{aligned}$$

Accordingly the permanent magnetism is represented by a portion of a parabola whose axis is parallel to that of Y. It

vanishes for $\alpha=0$, $\beta=0$ (as could be foreseen from the properties of the irons α and β , which have served as the grounds of the argument), and is a maximum for $\alpha=\beta$.

The number of the particles capable of remaining polarized after the interruption of the magnetizing force will at most form a quarter of the whole mass of the iron.

If the magnetizing force be too feeble to produce saturation, the lines OA, OrX will take up a position indicated approximately by the dotted lines.

These considerations agree fairly well with many observed facts.

Thus all causes which tend to open, even temporarily or only in certain directions, the network of the iron β (expansion, shocks, vibrations) set at liberty some of the polarized particles of α , and diminish the permanent magnetism.

The greater the proportion of β iron the more difficult becomes the polarization of α , in the diminished pores, and the greater must the magnetizing force be to produce saturation.

When the proportion of carbon or of manganese is so great that the whole of the iron on quenching or even without this takes up the state β , a substance will result which is incapable of taking up magnetism; for example Spiegel-iron containing 25 per cent. of manganese and upwards, and Hadfield's steel. Since hardening takes place more energetically at the surface than in the interior of a bar, the relation $\frac{\alpha}{\beta}$ will always be smaller there. The permanent magnetism remaining after saturation will therefore be stronger at the surface if $\alpha > \beta$, which is the common case. It would be more feeble if $\beta > \alpha$.

Magnets formed of laminae are in general more powerful than those of the same volume in a single piece, because the laminae are more hardened. But the contrary should be the case with metals in too hard a condition.

It is difficult after a bar has been magnetized to saturation in one direction to bring it to a moment of the same value in an opposite direction, because certain particles of the α metal being held immovably cannot be displaced, &c.

The iron β can also be looked upon as a medium whose viscosity increases as its percentage in the mixture is greater.

We can compare these ideas with the experiment of Hughes, who has obtained permanent magnets by mixing iron filings and wax and melting the latter, which in setting held fixed the polarized portions of iron.

LXI. *Notices respecting New Books.*

Chemical and Physical Studies in the Metamorphism of Rocks, based on a Thesis (with Appendices) written for the Doctorate in Science in the University of London. By A. IRVING, D.Sc., B.A., F.G.S. 8vo. 138 pages. Longmans & Co., London.

ROCK-METAMORPHISM, considered from the chemical and physical side, introduces the subject, which, after a definition of "metamorphism," as here meaning "only changes in the internal structure of rock-masses," is divided into three divisions—*paramorphism*, *metatropy*, and *metataxis*. The first refers to *atomic*, that is chemical, changes; the second to *molecular*, that is physical, changes; and the third to *mechanical* conditions. In one case the process is, as it were, the dissociation of a molecule into atoms; in the next, the breaking up of a solid into a liquid and then into a gas, the cohesion of the mass being gradually overcome until it becomes divided into molecules; in the third case, we have molar division, by pressure, percussion, or grinding. Such a change in a rock as is due to the introduction of a new, or the removal of an old mineral, and referred by many to metamorphism, is here separately noticed as *hyperphoric change*.

I. Paramorphism, or mineral change, divides itself into—1. *Primary paramorphism* (Genesis of Rocks), which leads to the recognition of a universal glowing magma at an early stage of the Earth's Evolution:—2. *Secondary paramorphism*, brought about by the action of saline (marine) waters in producing secondary minerals, derived from the primary minerals of the rock and not altering the composition of the rock when tried by bulk-analysis. Examples referred to are separation-products in slates and shales,—siliceous cements in volcanic tuffs and sarsen stones,—calcite in some igneous rocks,—quartz in the quartz-porphyrries of Bozen,—facts published by Judd, Allport, Bonney, Becker, and others.

II. Metatropy is defined and illustrated. The conversion of coal into anthracite and graphite, with a slight change in chemical composition, may be metatropic; the formation of palagonite and hydrotachylite from the glass of basalts by hydration,—the change of anhydrite into gypsum, of arragonite into calcite by dry heat, and of calcite into arragonite by solution and heat,—the results of contact metamorphism by heat, as some grauwackes and shales into hornstone and porcellanite,—of coal into coke,—sandstone into quartzite,—and limestone into marble, are metatropic. *Poly-morphism* is included in metatropy; and this variation of crystalline form is brought about by:—1. Temperature, as with carbonate of lime; 2. Molecular water, as with native hydrates of alumina and in some silicates of copper; 3. An accessory mineral, as with carbonate of lime tainted with some carbonates of the alkaline earths; and here the author suggests that these may have the rhombic system of arragonite rather than the hexagonal for their

normal crystalline system ; he refers also to the concretions in the *Magnesian Limestone of Durham*.

The vitrification and devitrification of rock (*e.g.* obsidian and tachylite) belong to metatropy. Sulphur and phosphorus, each being allotropic, are taken in illustration, as also arsenious oxide, metaphosphoric acid, silica, borax, and calcium fluoride. The author states that with regard to devitrification the following inductions seem to be warranted:—1. The vitreous state of a body represents a more primitive and simple molecular structure, with a corresponding low degree of stability. 2. There is a *latent heat of vitrification*, the loss of this being accompanied by the building up of more highly complex and more stable molecules, with a tendency to assume a crystalline form. 3. In some cases hydration or dehydration, as the case may be, appears to be a factor in the process of devitrification.

The behaviour of artificial glasses under various conditions is next considered with respect to devitrification, also the behaviour of flint under certain conditions.

Viewing the relative densities of the different allotropic forms of the same mineral, the author states that, as the maximum density and stability of molecular structure is identified with the crystalline form, pressure, by way of compression, is favourable to crystallization. Pressure crushing a rock may allow freer access and circulation of water with minerals in solution, and so prepare the way for paramorphic changes, but cannot induce direct metatropic change—therefore, continues the author, mere deformation of rocks by pressure may have had too much attributed to it as a factor in metamorphism.

The passage of minerals through this solid-liquid “critical state” (*i.e.* the state in which they were neither solid nor liquid), as exemplified by certain flattened masses of quartz, is illustrated with facts observed by the author and others. The access of water to rocks along their junction-planes is noted, and the consequent decomposition of such rocks, which, if subsequently compressed in deep earth-movements, might present appearances considered to be characteristic of “regional metamorphism.” Hence the author remarks that sometimes the further inference is drawn—“that the Archæan schists, &c., may be only instances on a grander scale of such transitional development.”

III. Metataxis. 1. Cleavage is first considered, with critical observations on the theories of Mr. Harker and Mr. O. Fisher ; with the latter our author does not agree. Lateral pressure, continued after folding and faulting have been effected, is the acknowledged cause of cleavage, but the author does not regard the accessory crystalline minerals on the cleavage-planes of many slates as the result of paramorphic changes induced by the pressure.

2. Crumpling and gnarling of the folia of some gneisses and schists ; and 3. The Foliation of schists are briefly noted. 4. Metataxic work by solar and lunar tides in a primæval condition of the globe is suggested, thus “the feeble foliation of the fundamental

Gneiss " may have been associated with "the earliest *solar* tidal waves, and the more pronounced foliation of the Archæan schists with the subsequent *lunar* tidal waves of the magma." . . . "Then as now the tidal action would vary (within much wider limits, however) with the relative positions of the Sun, the Earth, and the Moon, the maximum effect being produced when the Moon was in 'meridian.' Pfaff (*Algern. Geol. als. ex. Wiss.* p. 188 *et seq.*) has discussed the action of tidal movements in the magma upon the earliest rind of the Earth, initiating the first permanent inequalities upon its surface. If the Archæan schists (taken as a whole) represent this first-formed rind, their materials as they accumulated *by precipitation from the heavy atmosphere* being bathed through and through with H_2O in a highly superheated condition, we seem to have at once an explanation both of the frequent recurrence of gneiss (in a subordinate degree) among the schists as a result of tidal movements, and of those lithological characters by which they have misled the Neptunists into regarding them 'as sediments.'" The author takes his favourite subject of glacier-ice as an example of the several results of the physical forces acting on such a magma.

IV. Hyperphoric change is illustrated by dolomitization, some amygdaloids, some masses of rock-salt, and the production of selenite from pyrites in fossiliferous clays.

V. Contact-metamorphism, combining paramorphic, metatropic, metataxic, and hyperphoric changes, is treated in stages—1. Direct effects of heat and pressure. 2. Effects of the circulation of superheated water between the intrusive mass and the adjacent rocks. 3. Changes following upon the cooling of the igneous intrusive mass.

The General Remarks treat of the meaning and application of several words relating to metamorphism and metaphoric rocks,—such words and applications as the author would or would not approve of; also of Archæan, Cambrian, and some other old rock-stages. In his Conclusions he insists on the complex nature of metamorphism, and the different processes by which the results are effected;—on the incomplete explanation hitherto given of "regional metamorphism:—that "uniformitarianism" really ought only to apply to the fact of the Earth having always been subject to the same universal laws as the other cosmical bodies;—and that the mass of the Earth and its Atmosphere has remained the same from the beginning. He accepts the theory that there was a *pre-oceanic* stage, and that the Archæan gneisses and schists were essentially *diagenetic*, rather than metamorphic; and warns us that "such phrases as 'the highly metamorphosed Archæan gneisses and schists' must be relegated to an obsolete nomenclature of geological science." The author winds up his Conclusions by stating that "as the mists and clouds thus disperse, our intellectual vision begins to descry a *boundary to geologic time*, and the physical geologist begins to feel that over this question he can join hands with the astronomer and the natural philosopher."

In the Appendices is presented a large mass of chemical notes, and of collected and original information bearing on the multifarious subject-matters of the foregoing pages.

This is a remarkable book, full to overflowing with carefully collected notes on every kind of metamorphosed rock, and results of personal research. The author's happy acquaintance with German literature has been utilized by him in getting every available German idea on metamorphism into his Essay; and indeed this is a valuable and praiseworthy feature, certainly bringing us nearer to our Continental brethren; for, though in micropetrology they are quoted often, yet in the broader field of rock-changes and the theories thereto belonging, their views, though known to those interested therein, have not been brought together so closely before. French and British geologists have not, it seems, helped the author much. With regard to the latter, some here and there get very "bad marks" indeed; he readily runs them down, and among their wreckage he floats high and disdainful. Indeed his egotism is very distasteful, and not least so when he quotes small observations made by himself in the field, as if no one else, not even the tyro and the amateur, had seen the common thing and been told of its evident lesson again and again; for instance, the selenite in clay near Grantham, &c.

The American Geologists he treats respectfully; and indeed he expresses regret at not having known more of Mr. T. Macfarlane, some of whose views, as well as some published by Dr. S. T. Hunt, he now finds that he has inadvertently taken as his own.

In this Essay, of course, we meet with many facts and ideas already well known to both teachers and students; but certainly some are put aside as insecure, and some are authenticated and more clearly defined than heretofore. This is work in the right direction, and our thanks are due to the industrious, and indeed enthusiastic, author, who has brought his chemical and physical knowledge to bear on the advancement of Geology, by the elucidation of the Earth's development, according to the views and theories that seem best to him after an earnest and conscientious study of rocks and rock-changes.

If the Second Edition be called for, and well it might, the author should, if possible, be less dogmatic, and endeavour to make himself less prominent in the language and style of the book;—he should incorporate his more important notes as far as possible in the text, and above all make a good Index of both names and things,—for this would be very valuable for reference to the many good facts and notions in the book, and to the observers and authors who have treated of them.

LXII. *Intelligence and Miscellaneous Articles.*

THE RADIANT ENERGY OF THE STANDARD CANDLE ; MASS OF METEORS. BY C. C. HUTCHINS.

THE following investigation was undertaken with the primary object of finding, if possible, more trustworthy data for determining the mass of shooting-stars ; but a reliable determination of the radiation of the standard candle cannot fail to be of value for other purposes.

The apparatus employed in making the measurements was my thermograph*, the constant of which was found in the two following ways.

First method.—A copper Leslie cube, holding about 3 kilog. of water, was placed behind an opening of 16 square centim. in a wooden screen, which opening was closed by a movable shutter, by opening which the thermograph, one metre distant, could be exposed to the radiation from the cube.

The following quantities were then determined :—dimensions of cube ; weight of water contained in cube ; water-equivalent of cube ; mean of the galvanometer-deflexions taken during the interval that the cube and its contents were falling 5° from a temperature about 65° above that of the air ; time in seconds occupied by the cube in falling the 5° as above.

Knowing these quantities, we can evidently compute in ergs per second the radiant energy passing through the square centimetre of surface containing the thermal junction, and such that it will produce a deflexion of one division of the galvanometer-scale. A number of trials showed that 16.9 ergs per second was the quantity required.

Second method.—The constant was found by passing the rays of the sun through openings of 0.394 and 0.23 centim. diameter, and observing the galvanometer-deflexions when the thermograph was exposed in the divergent beam at a point where the diameter of the beam was 4.2 centim., and then computing the deflexion for the undiminished sunlight. Simultaneously with the above measures the radiation of the sun was observed with Pouillet's pyrheliometer.

The mean of several sets of measures by this method gave the constant 17.02 : agreeing better than could have been expected with the results of the first method. The candle employed was the ordinary sperm candle, six to the pound. It burned in still air, without snuffing, 7.37 grm. per hour. The radiation of the candle was measured by placing it behind the screen in place of the cube employed in finding the instrumental constant, the exposures being made in the same manner as for the cube. The deflexion given varied very much with the length of the wick of the candle, constantly increasing for a half hour or more after lighting. It therefore was necessary to observe the deflexion at what was con-

* Proc. American Academy, 1889.

sidered to be an average condition of the candle-flame, that is about fifteen minutes after lighting, when a deflexion of 75 scale-divisions was obtained.

This number, multiplied by the constant previously found, gives the radiant energy which from the candle passes through each square centimetre of a surface everywhere one metre from the candle, provided we assume that the candle radiates equally in every direction. To find the total radiant energy, we must, as a first step, know the area of cross section of the candle-flame in a plane perpendicular to the direction of the flame to the opening of the thermograph. To learn this, an image of the flame was projected upon 400 square centim. of paper, taking care to have the projecting lens midway between the candle and paper. It was then easy to trace about the image of the flame with a pen; and this having been done ten times upon the same sheet, the whole sheet was weighed, and then the tracings cut from it and also weighed. In this manner the section of the candle-flame was found equal to 1.308 square centim.

We now have the whole radiant energy of the candle,

$$\epsilon = \frac{4\pi \times 100^2 \times 75 \times 17}{1.303} = 1.23 \times 10^8 \text{ ergs per second.}$$

To find what portion of this total energy lies in the visible spectrum could be satisfactorily accomplished only by measures made in every part of the spectrum of the candle. Such measures have been made by Langley* in the spectrum of an argand gas-lamp with a glass chimney. He finds 2.4 per cent. of the total radiant energy to be visible. It is easy to compare the candle with such a lamp. At a certain distance from the thermograph an argand lamp, whose light was that of ten candles, gave a deflexion of 238 scale-divisions. When the lamp was replaced by the candle the deflexion was 29. Hence we see that very nearly 2 per cent. of the radiant energy of the candle is visible; or the visible part is 2.46×10^6 ergs per second; about 10.9 ft.-lbs. per minute.

We may now proceed to find the mass of a meteor, first upon the supposition that its rays have the same ratio of visible to total energy as have those of the candle, and later correct, if possible, the value thus found.

Let the meteor at a distance of 50 miles have a light equal to that of Vega; let it continue for 2 seconds with a velocity of 25 miles per second. From the best data we find that if the meteor were at 1 metre distance, the log of its candle-power would be 3.9851. Hence to find the energy ϵ , we have:—

log candle-power	3.9851
log energy of candle	8.0899
log 2	0.3010

$$\log \epsilon \dots\dots\dots 12.3760$$

* Science, vol. i. p. 482.

We have for the mass, $m = \frac{2\epsilon}{v^2}$; and employing the data assumed above we find $m = 0.2936$ grm.

If the meteor in burning produce, for a given expenditure of energy, more light than does the candle, then a less mass than the one found would serve to produce the light given by the meteor. From what has been observed of the spectra of meteors, it is safe to conclude that their light is mainly due to incandescent vapours of the materials composing the meteors. It is also known that the spectra of these substances remain unchanged throughout very considerable changes of temperature, and we may therefore be permitted to draw conclusions from laboratory experiments upon these substances in the state of vapour.

A lump of the Emmett Co., Iowa, iron meteorite was placed upon the lower carbon of an arc-lamp and vaporized by the passage of the current. The light given by the meteor-vapour was found, on the average, equal to that of 40 candles. The galvanometer-deflexion by the meteor at a certain distance from the thermograph was 223.2 scale-divisions. At the same distance the candle gave a deflexion of 55.4 divisions. From this we see that, for a given expenditure of energy, the arc of meteor-vapour gives ten times the light of the candle. Dividing the value of m obtained above by 10, we have $m = 0.029$ grm. for the mass of a meteor giving the light of a star of the first magnitude, moving with nearly the parabolic velocity and lasting for two seconds.—*American Journal of Science*, May 1890.

OBSERVATIONS ON ATMOSPHERIC ELECTRICITY IN THE TROPICS.

BY F. EXNER.

In order to investigate the relations of atmospheric electricity to the moisture of the air within certain limits, the author has made observations of the fall of atmospheric potential in countries with high relative moisture, particularly in the Indian Ocean between Aden and Bombay, in Bombay itself, and in Ceylon both on the coast and in the interior. The measurements were made with the well-known transportable apparatus invented by the author. The present paper contains only the total material of observation in tables, which comprise the date and hour of the observation, the temperature, absolute and relative moisture, the fall of potential, and meteorological observations. The discussion of the conclusions to be drawn from these numbers is reserved for a second paper. It need only be mentioned that all the values of the fall of potential were positive. Near the coast the finely-divided spray arising from the breaking of the waves exerted an increased action on the fall of potential. On the other hand, measurements made in the course of this journey in Cairo and the vicinity showed that there the dust of the air exerted a lessening influence on the fall of potential, which with a strong wind was so marked that the sign of the fall of potential became negative.—*Wiener Berichte*, xviii. p. 1004 (1889); *Beiblätter der Physik*, xiv. p. 144.

INDEX TO VOL. XXIX.

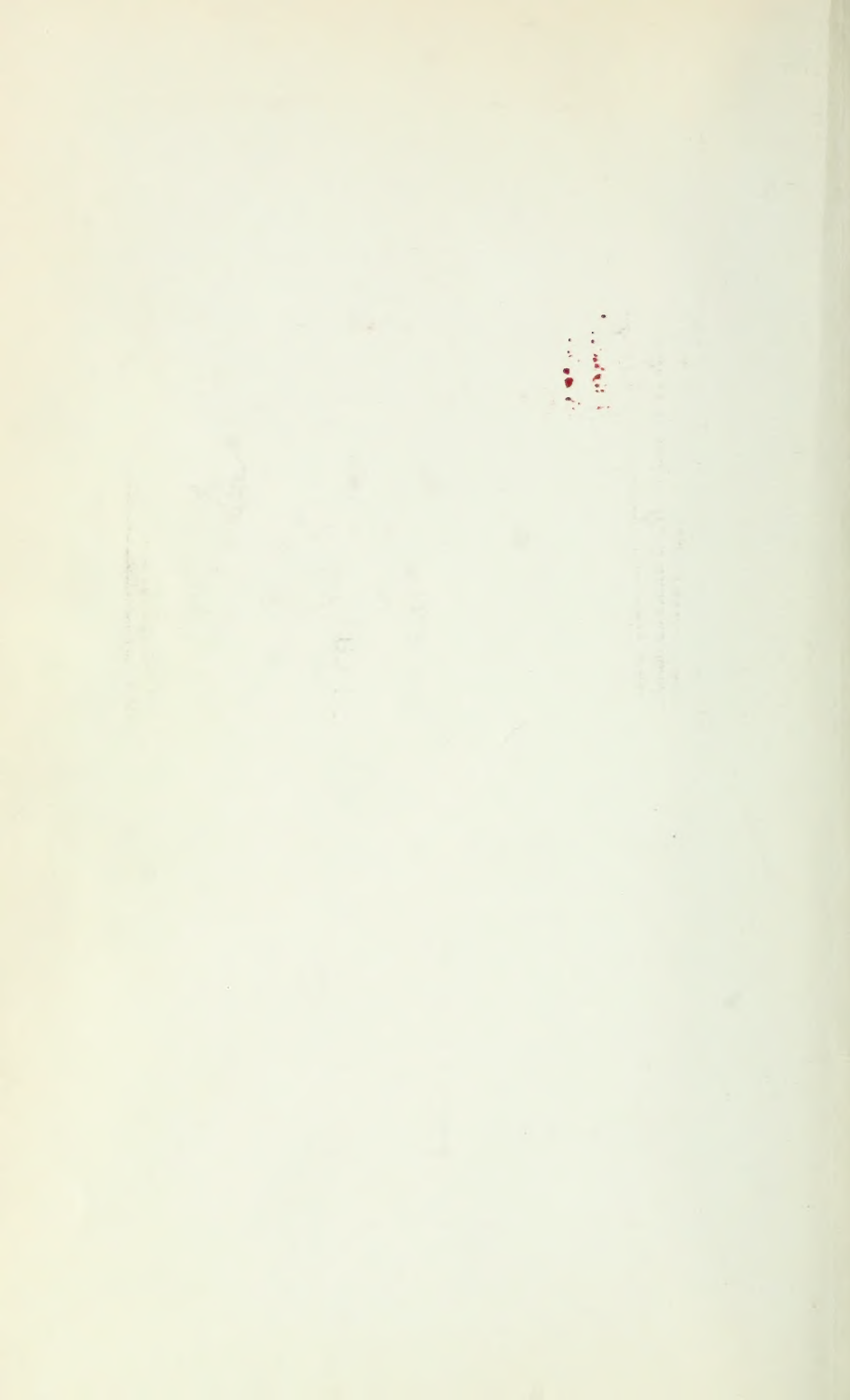
- ÆTHER**, on the non-existence of density in the elemental, 467.
- Air**, on a method of determining moisture and carbonic acid in, 306; on electrical vibrations in rarefied, without electrodes, 375; on the oscillations of periodically heated, 452.
- Atmosphere**, on the vibrations of an, 173.
- Atmospheric electricity in the Tropics**, on, 520.
- Barus (C.)** on the pressure-variations of certain high-temperature boiling-points, 141; on the change of the order of absolute viscosity encountered on passing from fluid to solid, 337.
- Bells**, on, 1.
- Bidwell (S.)** on the electrification of a steam-jet, 158; on the magnetization of iron in strong fields, 440.
- Bishop's ring**, on the nature of, 171.
- Boiling-points**, on the pressure-variations of certain high-temperature, 141.
- Bonney (Prof. T. G.)** on the crystalline schists of the Lepontine Alps, 284.
- Books, new**:—Fisher's *Physics of the Earth's Crust*, 211; *Transactions of the Edinburgh Geological Society*, Vol. VI. Part 1, 372; *Chrystal's Algebra*, Part II., 449; *Irving's Chemical and Physical Studies in the Metamorphism of Rocks*, 514.
- Brown (J.)** on dropping-mercury electrodes, 376.
- Calorimeter**, on a new form of mixing, 247.
- Candle**, on the radiant energy of the standard, 518.
- Carbonic acid in air**, on a method of determining, 306.
- Carnelley (Dr. T.)** on an algebraic expression of the periodic law of the chemical elements, 97.
- Carus-Wilson (C. A.)** on the behaviour of steel under mechanical stress, 200; on the distribution of flow in a strained elastic solid, 503.
- Chemical action and electrolytic conduction**, on the problems of, 383, 480.
- reactions, on the inert space in, 216.
- research, on a new method and department of, 401.
- Chronograph**, on a new form of electric, 377.
- Clouds**, on diffraction-colours with special reference to iridescent, 167.
- Coldridge (W.)** on the electrical and chemical properties of stannic chloride, 383, 480.
- Cole (G. A. J.)** on the variolitic rocks of Mont-Genèvre, 286.
- Contact-forces**, on the measurement of electromotive, of metals in different gases by means of the ultra-violet rays, 291.
- Coronæ**, on diffraction-colours with reference to, 167.
- Corpi (F. M.)** on the catastrophe of Kantzorik, Armenia, 133.
- Current**, on the time-integral of a transient electro-magnetically induced, 276.
- Currents**, experiment to prove the existence of the direct and inverse extra, 216.
- Curves**, on plotting, by the aid of photography, 180.
- Daguenet (C.)**: experiment to prove the existence of the direct and inverse extra-currents, 216.
- Diffraction-colours** with reference to coronæ and iridescent clouds, 167.
- Diffusion**, on evaporation and solution as processes of, 139.
- Dissociation in gases**, on the kinetic theory of, 18.
- Dubois (H. E. J. G.)** on Kerr's mag-

- neto-optic phenomenon, 253; on magnetization in strong fields at different temperatures, 293.
- Dunstan (Prof. W. R.) on an apparatus for the distillation of mercury in a vacuum, 367.
- Dymond (T. S.) on an apparatus for the distillation of mercury in a vacuum, 367.
- Electric chronograph, on a new form of, 377.
- current, on transient, produced by twisting magnetized iron and nickel wires, 123; on the direction of the induced, by twist when under longitudinal magnetizing force, 132; on the resistance of hydrogen and other gases to the, 214.
- radiation meter, on a new, 54.
- Electrical measuring-instruments, on the shape of movable coils used in, 434.
- oscillations in straight conductors, on, 450.
- resistance of iron, on the effect of repeated heating and cooling on the, 77.
- Electricity, on the disruptive discharge of, through gases, 182; on the passage of, through hot gases, 358, 441; on atmospheric, in the Tropics, 520.
- Electrification of a steam-jet, on the, 158.
- Electrifications due to the contact of gases with liquids, on, 56, 292.
- Electrodes, on the theory of dropping-mercury, 376, 479.
- Electrolytic conduction and chemical action, on the problems of, 383, 480.
- Electromagnetic waves, on the acceleration of secondary, 268.
- Elements, on an algebraic expression of the periodic law of the chemical, 97; on the structure of the line-spectra of the chemical, 331.
- Elster (Prof.) on the formation of ozone by the contact of air with ignited platinum, and on the electrical conductivity of air ozonized by phosphorus, 376.
- Enright (J.) on electrifications due to the contact of gases with liquids, 56.
- Exner (F.) on atmospheric electricity in the Tropics, 520.
- Flux (A. W.) on the form of Newton's rings, 217.
- Fog-bows, on the theory of, 453.
- Galvanometers, on sensitive, 208, 508.
- Gases, on the kinetic theory of dissociation in, 18; on electrifications due to the contact of, with liquids, 56, 292; on the disruptive discharge of electricity through, 182; on the resistance of, to the current and to electrical discharges, 214; on the passage of electricity through hot, 358, 441.
- Geitel (Prof.) on the formation of ozone by the contact of air with ignited platinum, and on the electrical conductivity of air ozonized by phosphorus, 376.
- Geological Society, proceedings of the, 133, 280.
- Gerard (Prof. E.) on plotting curves by the aid of photography, 180.
- Glaciation of the valleys of the Jhelam and Sind rivers, on the, 135.
- Glass, on the alteration in, produced by small variations of temperature, 289.
- Gore (Dr. G.) on a new method and department of chemical research, 401.
- Gray (Prof. A.) on sensitive galvanometers, 208.
- Gray (Prof. T.) on the effect of permanent elongation on the cross section of hard-drawn wires, 355.
- Gregory (J. W.) on the variolitic rocks of Mont-Genèvre, 286.
- Gregory (W. G.) on a new electric radiation-meter, 54.
- Haldane (Dr. J. S.) on a method of determining moisture and carbonic acid in air, 306.
- Hydrogen, on the resistance of, to the current and to electrical discharges, 214.
- Hutchins (C. C.) on the radiant energy of the standard candle, and on the mass of meteors, 518.
- Iron, on the effect of repeated heating and cooling on the electrical resistance of, 77; on the magnetization of, in strong fields, 440; on the Villari critical point of, 394.
- wires, on transient electric current produced by twisting magnetized, 123; on the direction of the induced current in, 132.

- Judd (Prof. J. W.) on the propylites of the Western Isles of Scotland, 287.
- Karsten (Prof. H.) on the geological age of the mountains of Santa Marta, 163.
- Kerr's magneto-optic phenomenon, on, 253.
- Langley (S. P.) on the temperature of the moon, 31.
- Liebreich (O.) on the inert space in chemical reactions, 216.
- Liquid, on two pulsating spheres in a, 113.
- Liquids, on electrifications due to the contact of gases with, 56, 292.
- Lodge (Prof. O. J.) on electrifications due to the contact of gases with liquids, 292.
- McConnel (J. C.) on diffraction-colours with special reference to coronæ and iridescent clouds, 167; on the theory of fog-bows, 453.
- Magnetism, on permanent, 511.
- Magnetization in strong fields at different temperatures, on, 293, 440.
- Magneto-optic phenomenon, on Kerr's, 253.
- Manganese steel, magneto-optic examination of, 304.
- Margules (Dr.) on the oscillations of periodically heated air, 452.
- Mather (T.) on the shape of movable coils used in electrical measuring-instruments, 434.
- Media, on texture in, 467.
- Mees (Prof. C. L.) on the effect of permanent elongation on the cross section of hard-drawn wires, 355.
- Mercury, on an apparatus for the distillation of, 367, 501.
- electrodes, note on dropping-, 376, 479.
- Metallic vapours, on the conductivity of, 441.
- Meteors, on the mass of, 518.
- Moon, on the temperature of the, 31.
- Morgan (Prof. C. Ll.) on the Pebidian of St. Davids, 282.
- Moser (J.) on electrical vibrations in rarefied air without electrodes, 375.
- Nagaoka (H.) on transient electric current produced by twisting magnetized iron and nickel wires, 123.
- Natanson (L.) on the kinetic theory of dissociation in gases, 18.
- Newton's rings, on the form of, 217.
- Nickel, on the Villari critical point of, 394.
- wires, on transient electric current produced by twisting magnetized, 123; on the direction of the induced current in, 132.
- and tungsten alloys, on the magnetism of, 136.
- Osmond (M. F.) on permanent magnetism, 511.
- Osmotic pressure, on the theory of, 490.
- Ostwald (Prof. W.) on the theory of dropping electrodes, 479.
- Ozone, on the formation of, by the contact of air with ignited platinum, and on the electrical conductivity of air ozonized by phosphorus, 376.
- Pembrey (M. S.) on a method of determining moisture and carbonic acid in air, 306.
- Periodic law of the chemical elements, on an approximate expression of the, 97.
- Perry (Prof. J.) on twisted strips, 244.
- Photography, on plotting curves by the aid of, 180.
- Pickering (S. U.) on a new form of mixing-calorimeter, 247; on the alteration in glass produced by small variations of temperature, 289; on the theory of osmotic pressure and its bearing on the nature of solutions, 427, 490.
- Prestwich (Prof. J.) on the Westleton beds of Norfolk and Suffolk, 280.
- Propylites of the Western Isles of Scotland, on the, 287.
- Puluj (Dr. J.) on a telethermometer, 291.
- Pumps, on the application of hydraulic power to mercurial, 138.
- Quaternions, on the importance of, in physics, 84.
- Radiation meter, on a new electric, 54.
- Rayleigh (Lord) on bells, 1; on the vibrations of an atmosphere, 173.
- Righi (Prof. A.) on the measurement of electromotive contact-forces of metals in different gases by the ultra-violet rays, 291.
- Runge (Prof. C.) on coincidences between the lines of different spectra, 462.

- Rydberg (Dr. J. R.) on the structure of the line-spectra of the chemical elements, 331.
- Santa Marta, on the geological age of the mountains of, 163.
- Schuster (A.) on the disruptive discharge of electricity through gases, 182.
- Selby (A. L.) on two pulsating spheres in a liquid, 113.
- Sheldon (S.) on the magnetism of nickel and tungsten alloys, 136.
- Smith (Rev. F. J.) on the application of hydraulic power to mercurial pumps, 138; on a new form of electric chronograph, 377; on a mercury-still for the rapid distillation of mercury in a vacuum, 501.
- Solid, on the distribution of flow in a strained elastic, 503.
- Solutions, on the nature of, 427, 490.
- Spark, on the heat developed in the, 214.
- Spectra, on the structure of the line, of the chemical elements, 331; on real and accidental coincidences between the lines of different, 462.
- Spheres in a liquid, on two pulsating, 113.
- Stannic chloride, on the electrical and chemical properties of, 383, 480.
- Steam-jet, on the electrification of a, 158.
- Steel under mechanical stress, on the behaviour of, 200.
- Stefan (Prof. J.) on evaporation and solution as processes of diffusion, 139; on electrical vibrations in straight conductors, 373, 450.
- Stiffe (Capt. A. W.) on the glaciation of the valleys of the Jhelam and Sind rivers, 135.
- Stoney (G. J.) on texture in media, and on the non-existence of density in the elemental æther, 467.
- Strips, behaviour of twisted, 244.
- Tait (Prof.) on the importance of quaternions in physics, 84.
- Telethermometer, on a, 291.
- Thomson (Prof. J. J.) on the passage of electricity through hot gases, 358, 441.
- Thomson (Sir W.) on the direction of the induced longitudinal current in iron and nickel wires by twist when under longitudinal magnetizing force, 132; on the time-integral of a transient electromagnetically induced current, 276.
- Threlfall (Prof. R.) on sensitive galvanometers, 508.
- Tomlinson (H.) on the effect of repeated heating and cooling on the electrical resistance of iron, 77; on the Villari critical points of nickel and iron, 394.
- Torsion and detorsion of metal wires, on the changes of temperature resulting from the, 140.
- Trouton (F. T.) on the acceleration of secondary electromagnetic waves, 268.
- Trowbridge (J.) on the magnetism of nickel and tungsten alloys, 136.
- Tungsten and nickel alloys, on the magnetism of, 136.
- Vibrations of an atmosphere, on the, 173.
- on electrical, in straight conductors, 373; in rarefied air without electrodes, 375.
- Villari (E.) on the resistance of hydrogen and other gases to the current and to electrical discharges, and on the heat developed in the spark, 214.
- Villari critical points of nickel and iron, on the, 394.
- Viscosity, on the change of the order of absolute, encountered on passing from fluid to solid, 337.
- Wassmuth (Dr. A.) on the changes of temperature resulting from the torsion and detorsion of metal wires, 140.
- Wires, on the changes of temperature resulting from the torsion and detorsion of metal, 140; on the effect of permanent elongation on the cross section of hard-drawn, 355.
- Worth (R. N.) on the igneous constituents of the Triassic breccias and conglomerates of S. Devon, 134.

END OF THE TWENTY-NINTH VOLUME.



BINDING LEFT JUN 15 1959

QC

1

P4

ser.5

v.29

Physical &
Applied Sci.
Serials

The Philosophical magazine

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY
